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Photochemistry of 1,1-dicyano-1-alkenes General aspects

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Abstract

The chemical behaviour of 32 selected 1,1-dicyano-1-alkenes (DCNA) that are devoid of additional unsaturation and of additional hetero-atoms, upon direct excitation by continuous irradiation with light of 253.7 nm wavelength into the long-wavelength flank of their longest wavelength UV absorption band has been studied in solvents ranging from cyclohexane to methanol. The predominant reaction products in the majority of cases were 1,1-dicyano-cyclopropanes formed via 1,2-migration of either hydrogen or methyl/alkyl from C-3 to C-2 (olefin to cyclopropane photorearrangement, OCPR). Photoreactions competing with OCPR were hydrogen atom abstraction from solvent by the C-2 of the DCNA and, in characteristically favourable cases only, 3,4-C–C bond cleavage. In cases of low OCPR quantum yields, hydrogen abstraction from solvent was dominant in cyclohexane or methanol but it could be suppressed by the choice of a solvent (methylene chloride, acetonitrile, *tert*-butanol) that more strongly resisted hydrogen abstraction. Further minor by-products were isomeric DCNA and 1,1-dicyano-3-alkenes. No carbene-derived products were observed. Supplementary experiments included quenching experiments and an investigation of the DCNA triplet state. The DCNA triplet state was formed at only ca. 1% on direct irradiation but it could be efficiently produced by sensitisation with benzophenone; in the absence of olefins as inter- or intramolecular substrates, it was fairly unreactive. All observed reactions occur from the lowest excited DCNA singlet state. According to the quenching experiments, this state is short-lived as compared to diffusional movements. Other than OCPR which appears to be due to cationic reactivity at C-2 exhibited by the perpendicular geometry of the excited double bond, hydrogen abstraction and 3,4-C–C bond cleavage appear to be due to radical reactivity at C-2 exhibited by geometries of the excited double bond that are intermediate between planar and perpendicular and are due to vibration about the perpendicular conformation.

Keywords: Photoisomerisation; 1,2-Shift; Cyclopropane; Electron-deficient olefin; Excited singlet state

1. Introduction

There exist many reports on the photoreactions of directly excited 1-alkene-1,1-dicarbonitriles (1,1-dicyano-1-alkenes, DCNA). All DCNA so far investigated, however, bear some additional double bonds or chromophores or heteroatoms in their molecules and these additional elements of structure determined the observed photochemistry. With one saturated C-atom between the DCNA chromophore and an extra C=C double bond, di-π-methane rearrangement was observed [1–3]. With two saturated C-atoms in-between, the dominant reactions on direct excitation were either formation of a five-membered ring [4] or cleavage of the central C–C single bond to give two allylic moieties which either ended up as two separate molecules or recombined to result in an overall 1,3-*trans*-position; [4–8] in one case, intramolecular [2 + 2] cycloaddition to form a bicyclo[2.2.0]hexane has also been observed [9]. On triplet sensitisation by benzophenone, the same systems reacted quite differently, affording bicyclo[2.1.1]hexanes by crossed intramolecular [2 + 2] cycloaddition [8]. In the presence of water and of electron acceptors that absorbed all light, still another reaction was dominant, namely, photo-induced single electron transfer oxidation of the additional C=C double bond by the photoexcited electron acceptors ultimately leading to ring-closure by intramolecular free-radical attack on the DCNA chromophore [10,11]. With DCNA in special unsaturated and strained molecular environments, special photoreactions were observed [12–14]. Towards electron donating chromophores in the same molecule, the DCNA moiety has served as an electron acceptor in intramolecular photochemical single electron transfer [15–17]. To mention at last, there exists abundant literature on DCNA that are conjugated to other chromophores; their photoreactions are not characteristic of the DCNA chromophore.

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To the best of our knowledge, there has been no report on the photochemistry of DCNA lacking additional chromophores, C=C double bonds, and heteroatoms in their molecules ("lone" DCNA). In the following, we wish to present that report.

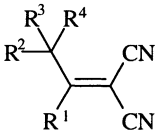
2. Experimental

2.1. General

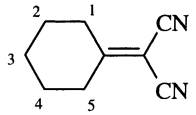
Solvents for irradiations were spectroscopic grade (Merck), in case of *tert*-butanol "puriss" (Fluka). Solvents for chromatography were technical grade and were distilled through a reflux condenser before use. Preparative chromatographic separations used silica gel, 0.04–0.063 mm (Merck) and an automatic fraction collector "Super Frac" (Pharmacia Biotech). Reagents were of the purest quality from Fluka, Aldrich, or Merck and were used as received. NMR spectrometer: Bruker AM 400, operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Detailed NMR data of all new compounds are presented in Appendix A. Quantitative capillary g.l.c. used mostly cyanopropylphenyl (14%) plus dimethyl (86%) polysiloxane (RTX 1701) as the absorbent and temperature-programming.

2.2. Preparation of DCNA

All DCNA (Scheme 1) except **1b7** were prepared by Knoevenagel condensation from the respective carbonyl compounds and malononitrile. The following DCNA used in the present work have been reported in the literature: **1a1** [18], **1a2** [19], **1a3** [20], **1a6** [21], **1a7** [22], **1a10** [23], **1a11** [24], **1a12** [25], **1b1**–**1b3** [26], **1b5**–**1b6** [27], **1b9**–**1b12** [26], **1b13**–**1b16** [28], **1b17** [29], **1b18** [30], and **1b20** [31]. The procedure used by us was either that given for a particular DCNA in the literature, or the standard procedure [26], or, in the case of sensitive carbonyl compounds (such as primary aldehydes), preferably the following. To a solution of 0.6 mol aldehyde or ketone and 0.6 mol malononitrile in 400 ml dry toluene or dichloromethane was added 100 g "Plaster of Paris" and the slurry was stirred at room temperature under exclusion of atmospheric moisture for 48 h. Filtration, washing the solids with ether, removal of solvent from the combined solutions, and distillation of the residue at <1 Torr furnished the DCNA in >80% yield and >95% purity according to ^{1}H NMR and UV spectroscopy. If crystalline, the DCNA were recrystallised from ethanol, ether petrol ether, or pentane at −70 °C. The preparation of **1a5** is described in a separate paper [32].



		R^1	R^2	R^3	R^4
1a1	(**9**)	H	H	H	H
1a2	(**5**)	H	H	H	Me
1a3	(**6**)	H	H	H	*i*Pr
1a4	(**7**)	H	H	H	*t*Bu
1a5	(**8**)	H	H	H	Allyl
1a6	(**1**)	H	H	Me	Me
1a7	(**2**)	H	H	Me	*t*Bu
1a8	(**3**)	H	H	*cis*-CHMe$(CH_2)_4$	
1a9	(**4**)	H	H	*trans*-CHMe$(CH_2)_4$	
1a10		H	H	$(CH_2)_2$	
1a11		H	H	Ethylidene	
1a12	(**23**)	H	Me	Me	Me
1b1	(**21**)	Me	H	H	H
1b2	(**16**)	Me	H	H	Me
1b3	(**10**)	Me	H	Me	Me
1b4	(**11**)	Me	H	$(CH_2)_5$	
1b5		Me	H	$(CH_2)_2$	
1b6		Me	H	CH_2CMe_2	
1b7		Me	H	Ethylidene	
1b8		Me	H	2-Me-propylidene	
1b9	(**25**)	Me	Me	Me	Me
1b10	(**17**)	$(CH_2)_3$		H	H



1b11	(**18**)	(unsubstituted)
1b12	(**12**)	1-Me-
1b13	(**13**)	*seqcis*-1,4-di-Me-
1b14	(**14**)	*seqtrans*-1,4-di-Me-
1b15	(**15**)	*seqcis*-1,2-$(CH_2)_4$
1b16	(**67**)	*seqtrans*-1,2-$(CH_2)_4$
1b17	(**19**)	3-*t*Bu-
1b18	(**20**)	1,4-CH_2
1b19	(**62**)	1,5-$(CH_2)_3$
1b20	(**65**)	1,3,5-CH_2CHCH_2 CH_2

Compound numbers in parentheses refer to the accompanying paper [38]

Scheme 1.

2.2.1. 2-(3,3-Dimethyl-butylidene)-malononitrile (*1a4*)

From 3,3-dimethyl-butyraldehyde (Aldrich). Liquid, bp: 42 °C/0.007 mbar. UV (*n*-hexane): λ_{max} = 225 nm; $\varepsilon_{253.7\,nm}$ = 741.

2.2.2. 2-(2,3,3-Trimethyl-butylidene)-malononitrile (*1a7*)

From 2,3,3-trimethyl-butyraldehyde [33]. Mp: 31–33 °C; bp: 95 °C/1 mbar. UV (*n*-hexane): $\lambda_{max}(\log \varepsilon)$ = 228 nm (4.14); $\varepsilon_{253.7\,nm}$ = 1106.

*2.2.3. Cis- and trans-2-[(2-methyl-cyclohexyl)-methylene]-malononitrile (**1a8** and **1a9**)*

A *cis–trans* mixture of 2-methyl-cyclohexane carbaldehyde [34] was separated into the two components by preparative g.l.c.

*2.2.4. 2-[(Cis-2-methyl-cyclohexyl)-methylene]-malononitrile (**1a8**)*

From the *cis*-aldehyde [35]. Mp: 18–22 °C; bp: 78 °C/0.3 mbar. UV (*n*-hexane): $\lambda_{max}(\log \varepsilon) = 231$ nm (4.17); $\varepsilon_{253.7\,nm} = 2600$.

*2.2.5. 2-[(Trans-2-methyl-cyclohexyl)-methylene]-malononitrile (**1a9**)*

From the *trans*-aldehyde [36]. Liquid, 97% pure (contaminant 2.2% *cis*-epimer), bp: 67 °C/0.2 mbar. UV (*n*-hexane): $\lambda_{max}(\log \varepsilon) = 233$ nm (4.13); $\varepsilon_{253.7\,nm} = 2867$.

*2.2.6. 2-(1-Cyclohexyl-ethylidene)-malononitrile (**1b4**)*

From cyclohexyl-methyl-ketone (Fluka). Mp: 44–46 °C; bp: 94 °C/0.1 mbar. UV (*n*-hexane): $\lambda_{max}(\log \varepsilon) = 237$ nm (4.08); $\varepsilon_{253.7\,nm} = 6166$.

*2.2.7. 2-(1-Methyl-but-t-2-enylidene)-malononitrile (**1b7**)*

By irradiation (253.7 nm) of **1b5** in cyclohexane to complete conversion followed by purification by preparative g.l.c. Mp: 31–35 °C. UV (*n*-hexane): $\lambda_{max}(\log \varepsilon) = 259$ nm (4.37); $\varepsilon_{253.7\,nm} = 23000$.

*2.2.8. 2-(1,4-Dimethyl-pent-t-2-enylidene)-malononitrile (**1b8**)*

From 5-methyl-hex-*t*-3-en-2-one [37]. Liquid, bp: 60 °C/0.1 mbar. UV (*n*-hexane): $\lambda_{max}(\log \varepsilon) = 280.5$ nm (4.38); $\varepsilon_{253.7\,nm} = 8462$.

*2.2.9. 2-(Bicyclo[3.3.1]non-9-ylidene)-malononitrile (**1b19**)*

From bicyclo[3.3.1]nonan-9-one (Aldrich). The crude product was not distilled but dissolved in ether, treated with charcoal, and after addition of petrolether crystallised at −70 °C. Mp: 85–86 °C, colourless. UV (*n*-hexane): $\lambda_{max}(\log \varepsilon) = 238.7$ nm (4.19); $\varepsilon_{253.7\,nm} = 8035$.

2.3. Preparative irradiations

2.3.1. General aspects

Irradiations used the unfiltered light of mercury lamps and quartz equipment opaque below 200 nm. Since the investigated DCNA were transparent above 270 nm, the principal exciting wavelength, therefore, was 253.7 nm with small contributions by 248 and 265 nm. The following setups were used: Rayonet reactor with eight low pressure mercury lamps and 120 W overall output, up to twelve 15-ml quartz tubes holding the reactant solution, flushed with argon before irradiation and closed with ground stoppers, evenly distributed in the interior of the reactor and cooled by air ventilation (method A); Rayonet reactor as before, one 50–800 ml quartz vessel with internal cooling by water supplied from a thermostat (method B); immersion well quartz apparatus with a concentrically placed 500 V, 100 W, low pressure mercury lamp made from Vycor glass (supplied by Gräntzel, Karlsruhe, Germany), with a concentric quartz cooling jacket between lamp and solution, cooled by water as before (method C); like method C, but using a 125 W high pressure mercury lamp (Philips HPK 125) (method D). Irradiations were carried to complete conversions (as monitored by g.l.c. or ^{1}H NMR) unless indicated otherwise.

2.3.2. Individual preparative irradiations

These are arranged according to DCNA numbers as given in Scheme 1.

*2-Cyclohexyl-2-ethyl-malononitrile (**4a1**)*: 0.9 g (9.8 mmol) **1a1**, 350 ml cyclohexane, 400 ml quartz vessel (method C), irradiation for 120 h. Distillation at 80 °C (bath) and 0.4 mbar furnished 300 mg distillate and a dark brown residue. The distillate consisted of 92.6% **4a1**, 6.2% **3a1**, and 1.2% **1a1** according to ^{1}H NMR and a small amount of **2a1** according to g.l.c.

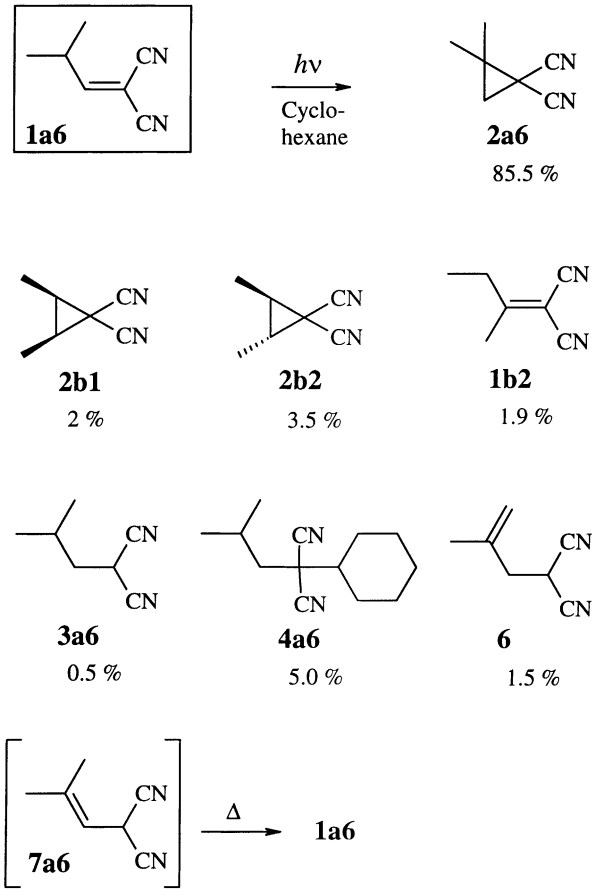
*2-Methyl-cyclopropane-1,1-dicarbonitrile (**2a2**)*: 0.6 g (5.6 mmol) **1a2**, 180 ml cyclohexane, 12 quartz tubes (method A), irradiation for 24 h. Distillation at 100 °C and 0.7 mbar gave 0.4 g crude (90% pure) **2a2**; dark distillation residue.

*2-Isopropyl-cyclopropane-1,1-dicarbonitrile (**2a3**)*: 4.0 g (30 mmol) **1a3**, 900 ml cyclohexane, five times 12 quartz tubes (method A), irradiation each time for 24. Distillation at 60–90 °C (bath) and 0.13 mbar gave 3.3 g distillate and a dark residue. Redistillation furnished 0.61 g fore-run followed by 2.07 g pure **2a3** which solidified to colourless crystals, mp: −2 to 3 °C.

*2-(1,1-Dimethylethyl)-cyclopropane-1,1-dicarbonitrile (**2a4**), 2-cyclohexyl-2-(3,3-dimethylbutyl)-malononitrile (**4a4**), and 2-(1,1-dimethylethyl)-2-vinyl-malononitrile (**10**)*: 2.0 g (13.5 mmol) **1a4**, 450 ml cyclohexane, twice 12 quartz tubes (method A), irradiation each time for 24 h. Distillation at up to 160 °C (bath) and 0.1 mbar furnished a distillate and a dark-brown residue. The distillate was subjected to preparative g.l.c. to furnish consecutively 162 and 236 mg unidentified mixtures containing no *tert*-butyl groups, 201 mg **10**, 459 mg **2a4**, 55 mg **4a1** (secondary photoproduct from **1a1**), 64 mg unidentified mixture, and 52 mg **4a4**.

The irradiation of **1a5** is described in a separate paper [32].

*2,2-Dimethyl-cyclopropane-1,1-dicarbonitrile (**2a6**) and 2-cyclohexyl-2-(2-methylpropyl)-malononitrile (**4a6**)*: 2.4 g (20 mmol) **1a6**, 300 ml cyclohexane, 400 ml quartz vessel (method C), irradiation for 66 h. Chromatography over 400 g silica gel with dichloromethane furnished, among minor fractions, consecutively 200.2 mg **4a6**, mp: 38–44 °C, and 1566.8 mg (65.2%) **2a6**, mp: 39–40 °C. On low conversions, quantitative capillary g.l.c. of the reaction mixtures showed the result presented in Scheme 2; sequence of retention of C_7



Scheme 2.

compounds on a low polarity silicon column (RTX-1701): **3a6**, **1a6**, **7a6**, **2a6**, **2b2**, **1b2**, **2b1**, **6**.

*2-(1,1-Dimethylethyl)-2-methyl-cyclopropane-1,1-dicarbonitrile (**2a7**) and 2-(1,1-dimethylethyl)-2-(E-propenyl)-malononitrile (**9**)*: 0.5 g (3 mmol) **1a7**, 500 ml *tert*-butanol, 800 ml quartz vessel (method C), irradiation for 1 h. Removal of solvent left 360 mg dark-brown material. Chromatography over 70 g silica gel with pentane and 2% ether furnished consecutively 62.1 mg impure (40%) **9**, 108.1 mg impure (50%) **2a7**, and 70.2 mg non-elucidated mixed fractions.

*3R*4S*- and 3S*4S*-4-methyl-spiro[2.5]octane-1,1-dicarbonitrile (**2a8** and **2a9**)*: 2360 mg (13.5 mmol) **1a9**, 360 ml *tert*-butanol, twice 12 quartz tubes, irradiation each time for 24 h. Removal of solvent and distillation at 80–110 °C (bath) and 0.2 mbar furnished 2324 mg of a colourless mixture of **2a8**, **2a9**, and minor components which was subjected to preparative g.l.c. to furnish 610 mg lower boiling fraction (**2a8**) and 305 mg higher boiling fraction (**2a9**). Crystallisations from ether at −23 °C yielded 288 mg **2a8**, mp: 38–42 °C, and 148 mg **2a9**, mp: 39–44 °C. A mixture of equal amounts of the two crystalline isomers at room temperature liquefied immediately.

*2-(E-but-2-enylidene)-malononitrile (t-**1a11**)*: 800 mg (6.78 mmol) **1a10**, 180 ml cyclohexane, 12 quartz tubes (method A), irradiation for 4 h. Removal of solvent and distillation of the reddish-brown residue at 100 °C (bath) and 1 mbar furnished 221 mg colourless distillate which solidified, mp: 35–40 °C (*t*-**1a11**).

*2,2,3-Trimethyl-cyclopropane-1,1-dicarbonitrile (**2b3**, method 1)*: 1.34 g (10 mmol) **1a12**, 100 ml cyclohexane, 100 ml quartz vessel (method D), irradiation for 66 h. Removal of solvent left 1477 mg of a semi-crystalline residue. Recrystallisation from petrol ether furnished 625.3 mg (46.8%) **2b3**, mp: 43–45 °C, colourless.

Photolysis of **1b2**: Photolyses in cyclohexane (method A), yielded **2b2**, **3b2**, **2b1**, and **4b2** in a ratio of (4.57 ± 0.4):(21.8 ± 2.2):(2.93 ± 0.3):(70.6 ± 10) (g.l.c. analyses; retention times increase in the sequence given).

*2,2,3-Trimethyl-cyclopropane-1,1-dicarbonitrile (**2b3**, method 2)*: 1.34 g (10 mmol) **1b3**, 90 ml cyclohexane, 100 ml quartz vessel (method B), irradiation for 142 h to partial conversion. Removal of solvent and separation of the residue by preparative g.l.c. afforded 563 mg unchanged **1b3** and 291 mg **2b3**, mp: 43–45 °C.

*2-Methyl-spiro[2.5]octane-1,1-dicarbonitrile (**2b4**)*: 1.0 g **1b4**, 100 ml cyclohexane, seven quartz tubes (method A), irradiation for 96 h. Removal of solvent and distillation at 100–120 °C (bath) and 0.05 mbar afforded 901.6 mg which on crystallisation from ether/petrol ether at −23 °C afforded 518 mg (51.8%) **2b4**, mp: 29–33 °C.

*2-(E-1-methyl-but-2-enylidene)-malononitrile (t-**1b7**)*: 1.21 g (9.17 mmol) **1b5**, 240 ml cyclohexane, twice eight quartz tubes (method A), irradiation for 168 h. Removal of solvent and distillation at 60–100 °C (bath) and 0.1 mbar gave 667 mg distillate which partially solidified and on crystallisation from ether/pentane furnished 300 mg *t*-**1b7**, mp: 29–32 °C.

*2,2,3,3-Tetramethyl-cyclopropane-1,1-dicarbonitrile (**2b5**), 2-cyclohexyl-2-(1,2,2-trimethylpropyl)-malononitrile (**4b9**), and 2-cyclohexylperoxy-2-(1,2,2-trimethylpropyl)-malononitrile (**8**)*: 3.0 g (20.2 mmol) **1b9**, 350 ml cyclohexane, 400 ml quartz vessel (method C), irradiation for 162 h. Removal of solvent left a brown residue which was chromatographed over 550 g silica gel with pentane and 2% ether to furnish consecutively 26.3 mg complex mixture, 53.1 mg **8** [m/z = 264 (CI–MS; M^+)], 702.7 mg crude **4b9**, 24.3 mg isomer of **4b9** [m/z = 232 (CI–MS; M^+)], 566.3 mg **1b9**, 704.1 mg mixture of **1b9** and **2b5**, and 821.2 mg crude **2b5**. Crystallisations of the crude **4b9** from pentane at −23 °C furnished 530.4 mg, mp: 56–58 °C [m/z = 232 (CI–MS; M^+)]. Crystallisation of the crude **2b5** from pentane furnished 660.3 mg, mp: 50–52 °C, raised to 53–54 °C by recrystallisation.

*2,2-Dicyclohexyl-malononitrile (**4b11**)*: 1.46 g (10 mmol) **1b11**, 90 ml cyclohexane, 100 ml quartz vessel (method B), irradiation for 143 h to incomplete conversion. Distillation at <100 °C (bath) and 0.3 mbar furnished 941.4 mg of a colourless liquid consisting mainly of unchanged **1b11**, of a

minor amount of **3b11**, and even less **2b7**. From the distillation residue, **4b11** was obtained by sublimation at 120 °C (bath) and 0.3 mbar, after recrystallisation from petrol ether 68.1 mg, mp: 114–115 °C.

*1-Methyl-bicyclo[4.1.0]heptane-7,7-dicarbonitrile (**2b8**) and 2-cyclohexyl-2-(2-methyl-cyclohexyl)-malononitrile (**4b12**)*: 1.6 g (10 mmol) **1b12**, 100 ml cyclohexane, seven quartz tubes (method A), irradiation for 165 h. Distillation at 0.05 mbar afforded two fractions, 780.2 mg at 60–100 °C (bath), and 434.6 mg at 140–160 °C (bath). Crystallisation of the lower boiling fraction from ether/petrol ether at −23 °C afforded 175.7 mg **2b8**, mp: 36–38 °C. Crystallisation of the higher boiling fraction from ether/petrol ether with the aid of active charcoal afforded 134.4 mg **4b12**, mp: 92–96 °C.

1S,4R*,6R*-1,4-dimethyl-bicyclo[4.1.0]heptane-7,7-dicarbonitrile (**2b9**)*: 804.6 mg (4.62 mmol) **1b13**, 120 ml *tert*-butanol, eight quartz tubes (method A), irradiation for 138 h. Distillation at 60–80 °C (bath) and 0.015 mbar afforded 625 mg distillate which on crystallisation from *n*-hexane at −23 °C afforded 389.3 mg **2b9**, mp: 35–38 °C.

1S,4S*,6R*-1,4-dimethyl-bicyclo[4.1.0]heptane-7,7-dicarbonitrile (**2b10**)*: 804.7 mg (4.62 mmol) **1b14**, 120 ml *tert*-butanol, eight quartz tubes (method A), irradiation for 138 h. Distillation at 60–80 °C (bath) and 0.015 mbar aforded 337.8 mg distillate containing 91.3% **2b10**.

1aS,4aR*,8aR*-decahydro-cyclopropa[d]naphthalene-1,1-dicarbonitrile (**2b12**) and 1aR*,3aR*,7aR*,7bS*-decahydro-cyclopropa[a]naphthalene-1,1-dicarbonitrile (**2b17**)*: 1.2 g (6 mmol) **1b15**, 180 ml *tert*-butanol, 12 quartz tubes (method A), irradiation for 125 h. The reaction mixture contained 54% **2b12** and 14% **2b17** (g.l.c. analysis) and was separated by preparative g.l.c. to furnish **2b12** (lower boiling) and **2b17** (higher boiling).

1aR,4aR*,8aS*-decahydro-cyclopropa[d]naphthalene-1,1-dicarbonitrile (**2b13**)*: 1.0 g (5 mmol) **1b16**, 100 ml cyclohexane, six quartz tubes (method A), irradiation for 96 h. Distillation at 80–120 °C and 0.014 mbar gave 717 mg crude **2b13**, after crystallisation from diisopropyl ether 335.2 mg, mp: 48–50 °C. The distillation residue consisted of one main product, presumably **4b16**.

1S,3S*,6R*- and 1S*,3R*,6R*-3-(tert-butyl)-bicyclo[4.1.0]heptane-7,7-dicarbonitrile (**2b11** and **2b16**), 2-[seqcis-4-(tert-butyl)-cyclohexyl]-malononitrile (c-**3b17**), 2-[seqtrans-4-(tert-butyl)-cyclohexyl]-malononitrile (t-**3b17**), 3-[4-(tert-butyl)-cyclohexyl]-5,5-dimethyl-2-oxo-tetrahydrofuran-3-carbonitrile (**5b17**), and 2-[1R*,2R*,4R*-2-(tert-butoxy)-4-(tert-butyl)-cyclohexyl]-malononitrile (**12**)*: 5.87 g (29 mmol) **1b17**, 1100 ml *tert*-butanol, 600 ml quartz vessel (two batches), cooling water temperature: 30 °C (method C), irradiation of each batch for 2 weeks. Distillation afforded 5.3 g, bp: 91–115 °C/0.13 mbar. On crystallisation from 100 ml *n*-pentane the distillate afforded 1730.6 mg **2b11**, mp: 97–100 °C. The mother liquor after removal of the solvent was chromatographed over 800 g silica gel with pentane and 2% ether to yield consecutively fractions I–IV, followed by elution with pentane and 5% ether to yield consecutively fractions V–VIII: 100 mg I, 376.4 mg II, 40.7 mg III, 1062.3 mg IV, 264.8 mg V, 509.4 mg VI, 38.7 mg VII, and 99.5 mg VIII. Fractions I, VII, and VIII were unidentified mixtures, III was unchanged **1b17**. Fraction II on crystallisation from ether/*n*-pentane at −23 °C furnished 247.3 mg c-**3b17**, mp: 86–88 °C; the mother liquor after removal of solvent contained 70% c-**3b17**. IV on crystallisation from *n*-pentane furnished another 612.1 mg **2b11**. The mother liquor after removal of solvent consisted of 8% 4-*tert*-butyl-cyclohexanone, 24.8% 5-*tert*-butyl-spiro[2.4]heptane-1,1-dicarbonitrile (two epimers; formed from photoexcited **1b17** in its twist-boat form by alkyl migration), 18.9% **2b16**, 24.6% **2b11**, and 6.7% **12** (arranged in order of increasing g.l.c. retention times). Preparative g.l.c. effected the separation of this mixture; however, **2b16** was obtained only 71% pure, the main contaminant (25%) being **2b11**. Fraction V on repeated crystallisation gave 61.6 mg *t*-**3b17**, mp: 113–115 °C; the mother liquors contained predominantly *t*-**3b17** and some **5b17**; the two components tended to co-crystallise. Fraction VI was a mixture of the two epimers of **5b17** and some *t*-**3b17**; repeated crystallisation afforded one 84:16 (mp: 92–94 °C) and one 40:60 mixture of the two epimers of **5b21** but no pure compound. The data lead to estimates for the overall yields: 41.8% **2b11**, 1.4% **2b16**, 6.3% c-**3b17**, 4.5% *t*-**3b17**, 6.3% **5b17**, 0.3% **12**.

1S,2S*,4R*,5R*-tricyclo[3.2.1.0^{2,4}]octane-3,3-dicarbonitrile (**2b18**) and 3-(bicyclo[2.2.1]hept-2-yl)-5,5-dimethyl-2-oxo-tetrahydro-furan-3-carbonitrile (**5b18**)*: 1.0 g (6.33 mmol) **1b18**, 1000 ml *tert*-butanol, 700 ml quartz vessel (two batches), cooling water temperature: 35 °C (method C), irradiation of each batch for 150 h. Removal of solvent and chromatography of the residue over 240 g silica gel with pentane and 5% ether yielded consecutively 156.4 mg various complex fractions, 95.2 mg unchanged **1b22**, 189.1 mg fraction I, 103.5 mg fraction II, 27 mg fraction III, and 230.8 mg various complex fractions. Fraction I was re-chromatographed over 70 g silica gel with pentane and 3% ether to yield consecutively 96 mg of a 2:1 mixture of **1b18** and **2b18**, 10.8 mg pure **2b18**, 29 mg of a complex fraction containing 20% **2b18**, and 30.9 mg **5b18** (minor epimer). Fraction II on crystallisation from ether at −23 °C furnished 63.2 mg **5b18** (major epimer), mp: 126–128 °C; found: C 71.85, H 8.21, N 6.22; $C_{14}H_{19}NO_2$ requires C 72.07, H 8.21, N 6.00. Fraction III contained equal amounts of the latter epimer and an unidentified substance.

*2-(Bicyclo[2.2.1]hept-2-yl)-2-cyclohexyl-malononitrile (**4b18**)*: 280 mg (1.77 mmol) **1b18**, 300 ml cyclohexane, 350 ml quartz vessel (method C), irradiation for 22 h. The reaction mixture (354 mg) was chromatographed over 100 g silica gel with pentane and 2% ether to yield consecutively 20.6 mg unidentified mixtures, 214.7 mg **4b18** (mp: 62–68 °C), 7.7 mg unidentified mixture, 21.2 mg isomer of **4b18**.

1aR,4aS*,7aS*-octahydro-cyclopropa[d]indene-1,1-dicarbonitrile (**2b14**) and 2-(bicyclo[3.3.1]non-9-yl)-2-cyclohexyl-malononitrile (**4b19**)*: (a) 553 mg (2.97 mmol) **1b19**, 50 ml cyclohexane, four quartz tubes (method A), irradiation for 146 h. The product mixture (622.6 mg) was distilled at 0.03 mbar to yield 233.4 mg colourless liquid at 80–100 °C (bath) and 255.4 mg colourless crystalline material at 140–160 °C (bath). The liquid on crystallisation from ether/*n*-pentane at −23 °C afforded 120.9 mg **2b14**, mp: 58–62 °C. The higher boiling fraction on crystallisation from ether/*n*-pentane at −23 °C afforded 175.8 mg **4b19**, mp: 116–117 °C. (b) 450 mg (2.42 mmol) **1b19**, 150 ml *tert*-butanol, nine quartz tubes (method A), irradiation for 137 h. The product mixture (521 mg) was crystallised from ether/*n*-pentane at −23 °C to furnish 242.6 mg (54%) **2b14**, mp: 58–61 °C.

*2-(2-Adamantyl)-2-cyclohexyl-malononitrile (**4b20**)*: 900 mg (4.55 mmol) **1b20**, 850 ml cyclohexane, 900 ml quartz vessel (method C), irradiation for 120 h. Distillation at up to 180 °C (bath) and 0.14 mbar and crystallisation of the distillate from ether at −23 °C furnished 822.6 mg **4b20**, mp: 129–131 °C.

2.4. Analytical irradiations

These were carried out following the procedure outlined in an accompanying paper [38]. Accordingly, the relative rates in Scheme 5 were determined by g.l.c. according to the method for determining relative quantum yields outlined in this paper.

2.5. Syntheses

2.5.1. Deuteriated analogues of *1a2*

The requisite deuteriated forms of propionaldehyde were prepared from the sodium salt of 2,2,5-trimethyl-[1,3] dioxane-4,6-dione (methyl Meldrum's acid, Fluka) by sequential treatment with sulfuric acid or deuterio-sulfuric acid (to give propionic acid), lithium aluminium hydride or deuteride (to give propanol), and pyridinium chlorochromate (to give propionaldehyde) following standard procedures.

2.5.2. *3R*4S*- and 3S*4S*-4-methyl-spiro[2.5]octane-1,1-dicarbonitrile (**2a8** and **2a9**)*

Method of Boldt [39,40]. A solution of 24.1 g (219 mmol) 1-methyl-2-methylene cyclohexane [41,42] and 8.4 g (58 mmol) bromo-malononitrile (Fluka) in 25 ml dichloromethane was placed in a 50-ml solidex glass immersion well-irradiation apparatus equipped with a 125 W high pressure mercury lamp (Philips HPK 125) and irradiated for 4 h. Then 11.2 ml (80 mmol) triethylamine was added slowly, giving rise to an exothermic reaction. After 1 h at room temperature, the solution was washed consecutively with aqueous HCl to remove all amine, and with water. After the removal of solvent from the dichloromethane layer, the residue was distilled at 60–90 °C (bath) and 0.014 mbar to furnish 9.75 g (56 mmol, 96%) of a mixture of **2a8** (80.9%) and **2a9** (18.6%). Repeated crystallisation from ether/*n*-pentane at −70 °C furnished pure **2a8**, mp: 38–42 °C.

Method of Annen [43]. A mixture of 8.0 g (50 mmol) **1b12**, 47.5 ml (880 mmol) nitromethane, 10.0 g (89 mmol) potassium *tert*-butoxide (Fluka), and 400 ml *tert*-butanol was refluxed for 1.5 h. The *tert*-butanol was removed by distillation, water (300 ml) was added, and the mixture was extracted several times with ether. The combined ether phases were washed with water, dried over $MgSO_4$, and the ether was evaporated to leave a residue which was distilled to give 7.6 g of a mixture composed essentially of **2a8** and **2a9**, bp: 68–84 °C/0.02 mbar. Repeated crystallisations from ether and pentane at −23 °C yielded 1.37 g **2a9**, mp: 41–45 °C. Preparative g.l.c. of the combined mother liquors afforded two fractions. Crystallisation of the lower boiling fraction from ether and pentane at −23 °C yielded 1.86 g **2a8**, mp: 41–44 °C. Similar crystallisation of the higher boiling fraction yielded 1.19 g **2a9**, mp: 39–46 °C.

2.5.3. *1S*,4S*,6R*-1,4-dimethyl-bicyclo[4.1.0]heptane-7,7-dicarbonitrile (**2b10**)*

Method of Boldt, as above for **2a8** and **2a9**, using 7.0 g (64 mmol) 1,4-dimethyl-cyclohex-1-ene [44], 8.4 g (58 mmol) bromo-malononitrile, 30 ml dichloromethane, and 9.0 ml (64 mmol) triethylamine. Distillation at 60–90 °C (bath) and 0.015 mbar gave 8.3 g colourless liquid containing 83.7% **2b10** (40 mmol, 68%) and 5.6% of one main impurity. Repeated crystallisations from ether and pentane at −23 °C furnished 688 mg, mp: 17–18 °C, consisting of **2b10** (95.4%) and the impurity (4.4%).

2.5.4. *2,2,3-Trimethylbutane-4,4-dicarbonitrile (**3b9**)*

A total of 33.4 g (225 mmol) **1b9**, dissolved in 350 ml ethanol, was subjected to catalytic hydrogenation in the presence of 100 mg 10% Pd on charcoal (Fluka) at ambient pressure and temperature. Hydrogen uptake became gradually slower but did not show a sharp decrease after uptake of one mol H_2 per mol substrate. It was discontinued after that point had been reached. The product was purified by distillation through a spinning-band column to yield 6.6 g **3b9**, bp: 50 °C/0.1 mbar, mp: 8 °C.

2.5.5. *2-(2-Methylcyclohexyl)-malononitrile (**3b12**)*

Prepared from **1b12** as described above for **3b9**. Mixture of both epimers (^{1}H NMR), liquid.

2.5.6. *2,2-Dicyclohexyl-malononitrile (**4b11**)*

To the solution of 2.64 g (40 mmol) malononitrile (Merck) in 40 ml dry dimethyl sulfoxide, 11.2 (100 mmol) potassium *tert*-butoxide (Merck) was added under stirring under an argon atmosphere. After the exothermic reaction had ceased, the solution of 16.3 g (100 mmol) cyclohexyl bromide (Fluka) in 20 ml dry dimethyl sulfoxide and 10 mg

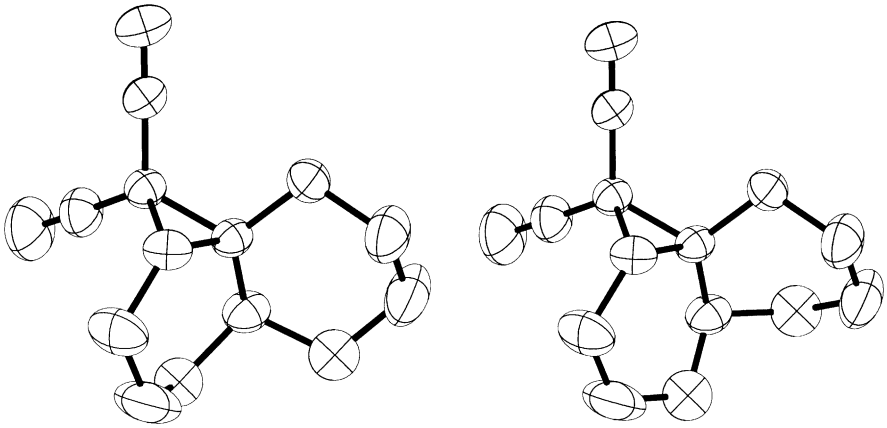


Fig. 1. Molecular structure of **2b13** as determined from X-ray crystallography. Two molecular conformations contribute in about equal amount. Thermal ellipsoids are drawn at the 50% probability level.

potassium iodide were added, and the mixture was stirred under argon at 80 °C for 50 h. After cooling to room temperature, water was added until complete dissolution of precipitated solids. Extraction with ether, drying of the ether phase with sodium sulfate, and evaporation of the ether left a residue that was distilled to afford 1.6 g dimethyl sulfoxide (bp: 50 °C/0.1 mbar) followed by a colourless liquid (bp: 140 °C/0.05 mbar) that crystallised. Two recrystallisations from petrol ether furnished 170 mg **4b11**, mp: 116–117 °C.

*2.5.7. 2-Methyl-but-1-ene-4,4-dicarbonitrile (**6**)*

A total of 8.0 g sodium hydride, 55% in mineral oil (Fluka, ca. 170 mmol) was placed in a 250-ml three-necked flask under an atmosphere of dry argon. *n*-Pentane was added in three portions under stirring and each portion removed from the flask by inverse filtration. Then 20 ml dry DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, Fluka) was added, followed by the dropwise addition of the solution of 11.0 g (167 mmol) malononitrile (Fluka) in 50 ml dry DMPU with external cooling by ice water. The latter addition was accompanied by a strong evolution of gas. Thirty minutes after completion of the addition, 15.0 g (166 mmol) 3-chloro-2-methyl-1-propene (methallyl chloride, Fluka) was added dropwise with cooling. After the exothermic reaction had ceased, stirring was continued at 40 °C for 2 h. Then 70 ml water was added at room temperature, followed by enough aqueous hydrochloric acid to acidify the aqueous phase. Several extractions with ether and countercurrent washing of the ether phases with water, drying of the combined ether phases with magnesium sulfate, and evaporation of the ether left a brown residue which was distilled at 42–62 °C/0.15 mbar to furnish 10.2 g of a mixture of unsubstituted mono-methallyl- (**6**), and of di-methallyl-malononitrile in comparable molar amounts (^{1}H NMR analysis). Fractional distillation yielded 4.0 g of an intermediate fraction, bp: 81–84 °C/5 mbar, containing 70% **6**.

*2.6. X-ray crystallography of **2b13** and **2b14***

The single crystals of **2b13** were obtained by crystallisation from hexane. The intensity data were collected on a Enraf-Nonius-CAD-IV diffractometer. The structure was solved by direct methods with SHELXS-97 [45]. The refinement was done with SHELXL-97 [45]. All non-hydrogen atoms were refined anisotropically except the disordered atoms C8A/B and C10A/B. Hydrogen atoms were included in structure factor calculations in their calculated positions. A summary of crystal data, experimental details, and refinement results are listed in Table 1. The molecular structure is shown in Fig. 1. The molecular structure is made up of two conformations in about equal amount, which gives rise to the disorder referred to above; both conformations are shown in Fig. 1.

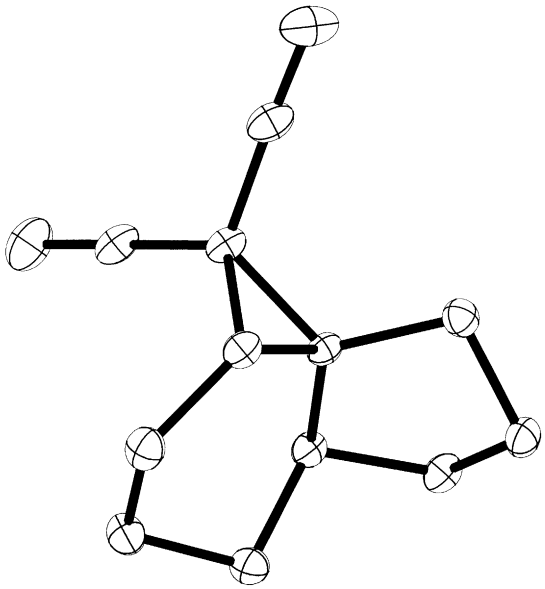


Fig. 2. Molecular structure of **2b14** as determined from X-ray crystallography. Thermal ellipsoids are drawn at the 50% probability level.

Table 1
Summary of crystal data, experimental details and refinement parameters for **2b13** and **2b14**

	2b13	**2b14**
Empirical formula	$C_{13}H_{16}N_2$	$C_{12}H_{14}N_2$
M_r (g/mol)	200.28	186.25
T (K)	293	100
Wavelength, (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$ (no. 19)	$P1$ (no. 2)
Unit cell dimensions		
a	6.2310(10) Å, $\alpha = 90^\circ$	6.9791(3) Å, $\alpha = 87.223(2)^\circ$
b	12.662(2) Å, $\beta = 90^\circ$	7.9466(3) Å, $\beta = 87.971(2)^\circ$
c	14.670(2) Å, $\gamma = 90^\circ$	9.2584(4) Å, $\gamma = 78.732(2)^\circ$
Volume (Å^3)	1157.4(3)	502.81(4)
Z	4	2
$D_{calc.}$ (mg/m^3)	1.149	1.230
Absorption coefficient (mm^{-1})	0.069	0.074
F_{000} (electron)	432	200
Crystal size (mm×mm×mm)	0.24 × 0.18 × 0.12	0.27 × 0.25 × 0.20
θ range for data collected (°)	2.12–29.88	2.20–33.80
Index ranges	$0 \le h \le 8$, $0 \le k \le 17$, $0 \le l \le 20$	$-9 \le h \le 10$, $-11 \le k \le 12$, $-14 \le l \le 10$
Reflections coll.	2094	5627
Independent reflections	1932 ($R_{int} = 0.0436$)	3367 ($R_{int} = 0.0264$)
Reflection with $I > 2\sigma(I)$	1171	2238
Absorption correlation	None	Empirical
Maximum and minimum transmission	–	1.000 and 0.891
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameter	1932/0/134	3367/0/183
Goodness-of-fit on F^2	1.150	0.992
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0571$, $wR^2 = 0.1710$	$R_1 = 0.0593$, $wR^2 = 0.1428$
R indices (all data)	$R_1 = 0.1206$, $wR^2 = 0.1962$	$R_1 = 0.0987$, $wR^2 = 0.1618$
Largest diffraction peak and hole, (electron/Å^3)	0.252 and −0.185	0.534 and −0.223

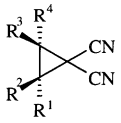
The single crystals of **2b14** were obtained by crystallisation from dichloromethane. The intensity data were collected on a Siemens SMART-CCD diffractometer. The structure was solved by direct methods using SHELXS-97 [45]. The refinement was done with SHELXL-97 [45]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found and refined isotropically. A summary of crystal data, experimental details, and refinement results are listed in Table 1. The molecular structure is shown in Fig. 2.

3. Results and discussion

3.1. General

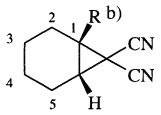
Scheme 2 displays the products formed on direct irradiation of the DCNA **1a6** in cyclohexane. The main product, **2a6**, is due to a 1,2-migration of a hydrogen atom in combination with a ring-closure. Formation of **2a6** is formally reminiscent of a "di-π-methane rearrangement", as has been observed with DCNA bearing an additional C=C double bond separated from the DCNA chromophore by one saturated C-atom [1–3], and which involves a 1,2-migration of a vinyl-type group. However, involving the active participation of the extra double bond [46], the di-π-methane rearrangement must be mechanistically quite different from the "olefin to cyclopropane photorearrangement" (OCPR) forming **2a6** from **1a6**. Also, **2b1** and **2b2** are OCPR products of **1a6** that result from methyl, rather than hydrogen, migration. Prompted by the behaviour of **1a6**, we subsequently investigated an array of selected DCNA the structures of which are displayed in Scheme 1. OCPR was found to be a fairly general reaction of directly excited DCNA lacking additional double bonds and electron lone pairs (called "lone" DCNA in the following). Scheme 3 displays the OCPR products obtained in course of the present work and Table 2 gives a qualitative survey of the results. The quantum yields for OCPR were found to range from 0.1 (for **2a6**) down to almost 0 depending on the structure type of the "lone" DCNA. They were virtually the same in solvents as different as cyclohexane, dichloromethane, acetonitrile, *tert*-butanol, and methanol, all of which are transparent at 253.7 nm. Formation of **1b2** and **6** (Scheme 2) is related to OCPR. The quantum yields and mechanism of OCPR as well as the formation of products related to OCPR will receive attention in a specifically devoted accompanying paper [38]. We shall also show there that **7a6** is only a very minor (primary) product.

3a6 and **4a6** (Scheme 2) are due to reaction of the photoexcited **1a6** with the solvent, cyclohexane. In contrast to



		R^1	R^2	R^3	R^4
2a1	(**34**)	H	H	H	H
2a2	(**30**)	H	H	H	Me
2a3	(**31**)	H	H	H	*i*Pr
2a4	(**32**)	H	H	H	*t*Bu
2a5	(**33**)	H	H	H	Allyl
2a6	(**26**)	H	H	Me	Me
2a7	(**27**)	H	H	Me	tBu
2a8	(**28**)	H	H	*t*[a)]-CHMe$(CH_2)_4$	
2a9	(**29**)	H	H	*c*[a)]-CHMe$(CH_2)_4$	
2b1	(**41**)	H	Me	Me	H
2b2	(**42**)	H	Me	H	Me
2b3	(**35**)	H	Me	Me	Me
2b4	(**36**)	H	Me	$(CH_2)_5$	
2b5	(**49**)	Me	Me	Me	Me
2b6	(**43**)	H	$(CH_2)_3$		H

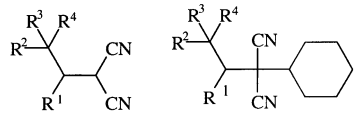
a) Me trans (*t*) or cis (*c*) relative to $C(CN)_2$



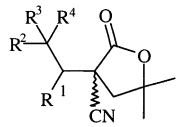
b) R = H unless indicated otherwise
c) α = on the side of the bridgehead atoms
β = on the side of the cyclopropane ring

2b7	(**44**)	(unsubstituted)
2b8	(**37**)	1-Me
2b9	(**38**)	1,4β-di-Me
2b10	(**39**)	1,4α-di-Me
2b11	(**47**)	3β-*t*Bu
2b12	(**40**)	1,2β-$(CH_2)_4$
2b13	(**68**)	1,2α-$(CH_2)_4$
2b14	(**64**)	1,2α-$(CH_2)_3$
2b15	(**45**)	2α-Me
2b16	(**50**)	3α-*t*Bu
2b17	(**46**)	2α,3α-$(CH_2)_4$
2b18	(**48**)	2β,5β-CH_2

Compound numbers in parentheses refer to the accompanying paper [38]



3 **4**



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(further specifying letters after "**3**", "**4**", and "**5**" in exact analogy to Scheme 1)

Scheme 3.

Table 2
Main products isolated after irradiation of individual DCNA with 253.7 nm light (excluding reaction with solvent)

DCNA	Main products	Efficiency[a]
1a1	**2a1**	B
1a2	**2a2**	A
1a3	**2a3**	A
1a4	**2a4**, **1a1**, **10**	A
1a5	**2a5**, **11**	A
1a6	**2a6**	A
1a7	**2a7**, **9**	A
1a8	**2a8**, **2a9**	A
1a9	**2a8**, **2a9**	A
1a10	**1a11**	A
1a12	**2b3**	A
1b1		D
1b2	**2b1**, **2b2**	C
1b3	**2b3**	B
1b4	**2b4**	B
1b5	**1b7**	A
1b6	**1b8**	A
1b9	**2b5**	B
1b10	**2b6**	C
1b11	**2b7**	C
1b12	**2b8**	B
1b13	**2b9**	B
1b14	**2b10**	B
1b15	**2b12**, **2b17**	C
1b16	**2b13**	B
1b17	**2b11**	C
1b18	**2b18**	C
1b19	**2b14**	B
1b20		D

[a] A: highly efficient, prevails over reaction with solvents; B: moderately efficient, prevails over reaction with unreactive solvents (*tert*-butanol, dichloromethane, acetonitrile), but reaction with reactive solvents (cylohexane, methanol) competes; C: poorly efficient, competes with reaction with unreactive solvents and with polymer formation; D: reaction with solvent and polymer formation only.

OCPR, the quantum yields for reaction of various DCNA with the solvent, cyclohexane, to give products analogous to **3a6** and **4a6** (Scheme 3) in general spanned a much narrower range, namely, 0.002–0.012 (see Table 1 of the accompanying paper [38]), without an obvious dependence on structure type; only for the particularly sterically hindered 2-*tert*-butyl-DCNA **1a12** and **1b9** these values dropped to 0.0016 and 0.0012, respectively. As a consequence, reaction with the solvents cyclohexane or methanol will prevail over OCPR for DCNA exhibiting low OCPR quantum yields. OCPR of many such DCNA nevertheless comes to bear in the solvents, dichloromethane, acetonitrile, and *tert*-butanol, all of which more strongly resist attack by photoexcited DCNA. Thus, the quantum yields for reaction with *tert*-butanol to form **5b17** and **5b18** (Scheme 3) were only 0.0001 and 0.0002, respectively. Quite generally for all directly excited DCNA, the quantum yields for polymer formation were about 0.001.

Directly excited "lone" DCNA bearing a *tert*-butyl group on C-3 or bearing a cyclopropyl group on C-2 have been

found to undergo another efficient reaction besides OCPR, namely, 3,4-bond cleavage (vide infra).

3.2. Photophysics, sensitised triplet chemistry, and SET quenching; the nature of the reactive state

"Lone" DCNA exhibit one single unstructured bell-shaped UV absorption band [17] extending from ca. 260–270 nm to the limits of the spectrometer at 200 nm and peaking at 222–235 nm ($\log \varepsilon = 4$) if the substituent on C-2 is hydrogen; if it is alkyl, the corresponding figures are 270–286, 200–210, and 228–241 nm ($\log \varepsilon = 4$–4.2); for some of the latter DCNA, the onset of a second absorption band below 200–210 nm was noticeable. Conjugation with cyclopropane causes red-shifts by about 20 nm; change from hexane to acetonitrile or methanol as the solvents causes red-shifts by only about 0–1 and 3 nm, respectively. We ascribe the band to a $\pi\pi^*$ transition fairly uncontaminated by other transitions. Both $n\pi^*$ (from the nitrogen lone pair) and Rydberg transitions are expected to keep well on the short-wavelength side of the band as estimated from the absorption spectra of non-conjugated nitriles and of differently substituted olefins, respectively. Irradiations were carried out at 253.7 nm throughout; that is, into the long-wavelength flank of the band. "Lone" DCNA show no luminescence [17].

In order to estimate the triplet energy of lone DCNA, we measured the rate constants for quenching of selected sensitiser triplet states by a representative DCNA, namely, **1a12**, in pulsed experiments. The results are shown in Table 3. They lead to an estimate of roughly 65 kcal/mol for the triplet energy of **1a12**. Sensitisers above this value are quenched by **1a12** at roughly diffusion-controlled rates while for those below this value the rates rapidly fall off with decreasing triplet energy. Accordingly, DCNA triplet photochemistry should be sensitised by benzophenone ($E_T = 69.1$ kcal/mol) the triplet state of which is quenched by **1a12** at a roughly diffusion controlled rate (Table 3). Indeed, as mentioned in Section 1, a DCNA bearing an additional C=C double bond separated from the DCNA chromophore by two saturated C atoms has been sensitised by benzophenone to afford a photoproduct different from that obtained on direct excitation; it involved the additional double bond [8]. An analogous photoproduct cannot be formed on sensitisation of a lone DCNA. When the prototypical lone DCNA **1a6** and **1a12** were irradiated (0.01 M, $\lambda > 280$ nm) in the presence of 0.03 M benzophenone in benzene, their only observed reactions were OCPR at quantum yields of 10^{-4}, that is, by almost 10^3 less than on direct excitation. Thus, apart from this very inefficient OCPR, the lowest triplet states of lone DCNA are unreactive in the absence of co-reactants. To be sure, they probably undergo efficient rotation about their C=C double bonds, but this rearrangement, being degenerate in the case of DCNA, escapes observation. We conclude that on direct excitation, the OCPR of DCNA occur from the lowest singlet ($\pi\pi^*$) state.

Table 3
Rate constants k for quenching of triplet states of selected sensitisers by **1a12** (methanol, 20 °C)

Sensitiser	E_T[a] (kcal/mol)	$k \times M$ (s)
Acetone	82	8×10^9
Xanthone	74	6×10^9
Benzophenone	69.1	4×10^9
Triphenylene	66.9	3.8×10^9
Phenanthrene	61.5	1.5×10^8
Naphthalene	60.9	2×10^8
Chrysene	57.1	1.5×10^7
2-Nitronaphthalene	56.9	5×10^6
1-Nitronaphthalene	55.1	2×10^7
Fluorenone	50.3[b]	$<5 \times 10^6$
Benzanthrone	46	$<1 \times 10^6$

[a] Triplet energy of sensitiser.
[b] Solvent: benzene.

In order to study the reactivity of triplet **1a12** towards an olefin, a solution of 0.1 M **1a12**, 0.084 M benzophenone, and 2 M cyclopentene in dichloromethane was irradiated with $\lambda > 280$ nm until the disappearance of most of the benzophenone by its photoreaction with the olefin [47]. Besides unchanged **1a12** (22%), no OCPR product but higher molecular-weight nitrogen-containing material and ca. 7% of the two epimers of 2-(2-cyclopenten-1-yl)-2-neopentyl-malononitrile were obtained. The latter obviously arose via abstraction of an allylic hydrogen atom of cyclopentene by triplet **1a12** followed by combination of the resulting radical pair.

The E_T value for the relaxed triplet of **1a12**, presumably featuring a perpendicular conformation of C-2 with respect to C-1, will be lower than that (ca. 65 kcal/mol) estimated above for the "spectroscopic" triplet of **1a12** but it may still be higher than that for *E*-1,3-pentadiene ("*t*-pip"; $E_T = 59.2$ kcal/mol). When **1a12** was irradiated with light of $\lambda = 253.7$ nm in cyclohexane in the presence of *t*-pip at various concentrations ([***1a12***] = 0.2 and 0.88 M; [*t*-pip] = 0.01–0.17 M) such that **1a12** absorbed >98% of the light, *E* to *Z* isomerisation of *t*-pip much in excess over that expected for direct excitation of *t*-pip was observed. No quenching of OCPR was observed. The following reaction scheme is assumed. The excited singlet state of **1a12** generated by direct excitation undergoes three competing unimolecular reactions. Return to the electronic ground state, OCPR, and intersystem crossing. The triplet state of **1a12** generated by the latter reaction undergoes competing unimolecular return to the electronic ground state and bimolecular triplet energy transfer to *t*-pip. The triplet pip thus generated decays to *Z*- and *E*-1,3-pentadiene. In addition, directly excited *t*-pip also forms *Z*-1,3-pentadiene. No exciplex formation between **1a12** and *t*-pip is assumed since the absorption spectra of their mixtures appear additive; moreover, OCPR is not quenched by *t*-pip. This scheme translates into an equation as

follows:

$$[t\text{-pip}] = a \times \Phi_{isc} + (\tau k_q)^{-1}, \quad (1)$$

where Φ_{isc}, τ, and k_q are the quantum yield for formation of the **1a12** triplet state by intersystem crossing, the natural lifetime of the **1a12** triplet state, and the rate constant for triplet energy transfer from the **1a12** triplet state to *t*-pip, respectively and $a = [\mathbf{1a12}] \times {}^3\Phi_{E\rightarrow Z} \times (b \times \Phi_{OCPR} - {}^1\Phi_{E\rightarrow Z} \times \varepsilon_{t\text{-pip}}/\varepsilon_{\mathbf{1a12}})^{-1}$. All constant quantities contained in a are known: ${}^3\Phi_{E\rightarrow Z}$ (0.44 [48]) and ${}^1\Phi_{E\rightarrow Z}$ (0.083 [49]) are the quantum yields for *E* to *Z* isomerisation of *t*-pip in its triplet state and on direct excitation, respectively, Φ_{OCPR} is the quantum yield for OCPR of **1a12** (0.043), and ε are absorption coefficients at 253.7 nm (*t*-pip: 50; **1a12**: 706). The variable b is the observed ratio of *E* to *Z* isomerisation of *t*-pip over OCPR, divided by the ratio of the concentrations of the substrates *t*-pip and **1a12**. Linear regression according to Eq. (1) yielded the parameters $(\tau k_q)^{-1} = 0.034 \pm 0.029$ M and $\Phi_{isc} = 0.011 \pm 0.003$ ($P = 0.95$). While this says little about τ and k_q, we can conclude that only a small amount (ca. 1%) of the directly photoexcited **1a12** passes into the triplet state. As mentioned above, qualitatively the same conclusion had been obtained for a DCNA featuring an additional C=C double bond separated from the DCNA chromophore by two saturated C atoms [8].

No band due to a CT-complex appears in the absorption spectra of mixed solutions of **1b12** and triethylamine (TEA) up to 40% TEA in hexane but it may be hidden under the main band of **1b12**. Anyway, OCPR of **1b12** and of other DCNA in cyclohexane is quenched by TEA, whereby part of the DCNA becomes hydrogenated at its C=C double bond. The obvious mechanism is single electron transfer from TEA (TEA/TEA$^+$: $E_{1/2} = 0.78$ V versus SCE in acetonitrile [50]) to excited singlet DCNA (**1b1**$^-$/**1b1** (in its electronic ground state): $E_{1/2} = -1.7$ V versus SCE in acetonitrile [51,52] in analogy to closely related systems [17,52]). Hydrogenation is triggered if a proton follows the transferred electron from TEA to DCNA. The dehydrogenated TEA (an enamine) thus ultimately formed undergoes messy dark reactions with DCNA which discolour the solutions and limit quantitative studies of the quenching reaction. Nevertheless, for **1b12**, such a study was possible with volume fractions of TEA ranging from 0.1 to 0.91 (i.e. 10–91% TEA; **1b12** accounted for >95% of the absorbed 253.7 nm light) if conversions were kept low enough so that the amounts of all photoproducts were proportional to irradiation time. The quenching was found to obey Perrin's law [53] [1]

$$\ln\left(\frac{\Phi_0}{\Phi}\right) = (2.9 \pm 0.5) f \quad (P = 0.95),$$

where Φ_0 and Φ are the quantum yields for OCPR in the absence and in presence, respectively, of TEA, and f is the volume fraction of TEA. Since Perrin's law is obeyed when the natural lifetime of the quenched species is short relative to diffusion and rotation of molecules (whereas the Stern–Volmer law is obeyed when the opposite is true), this indicates a very short natural lifetime of the quenched DCNA excited singlet state. The fraction of the quenched **1b12** molecules that become hydrogenated, increases steadily from 0.07 at $f = 0.02$ to 0.54 at $f = 0.91$. This indicates that not only such TEA molecules can quench that are in immediate contact to the excited **1b12** but also more distant ones which cannot transfer a proton to **1b12** after the electron transfer but instead will claim their electron back leaving behind ground-state **1b12**. (Note that the average distance of the TEA molecule closest to the excited **1b12** of all TEA molecules—which is the one most likely to quench—will increase with decreasing TEA concentration.)

The quantum yields for OCPR appeared independent of DCNA concentration (up to 1 M) both in cyclohexane and in methanol, indicating that there is no quenching of the reactive excited DCNA singlet state by ground-state DCNA molecules.

Atmospheric oxygen was found not to interfere with OCPR and its competing photoreactions on direct excitation to low conversions. This again demonstrates the short lifetimes of the involved excited species.

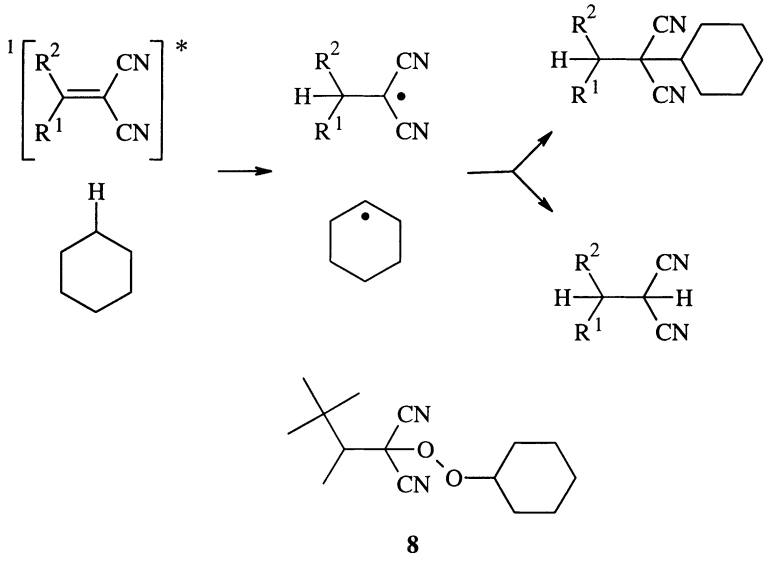
3.3. OCPR

An accompanying paper [38] will be specifically devoted to this reaction.

3.4. The reaction with solvent

Photoreaction with the solvent cyclohexane to furnish products **3** and **4** (Schemes 2–6) occurs with almost all DCNA studied, the exceptions being the 2-cyclopropyl DCNA, namely, **1a10**, **1b5**, and **1b6**. The hydrogenation products **3** are found at about one-tenth to one-fourth the amounts of the addition products **4**. In those cases where two epimeric **3** and two epimeric **4** are possible, both epimers are found in ratios between 1:1 and 1:10. The obvious mechanism for formation of **3** and **4** is abstraction of an H atom from the cyclohexane molecule by the C-2 atom of the photoexcited 1,1-dicyano-1-alkene chromophore to yield a cyclohexyl/alkyldicyanomethyl radical pair which then either collapses to **4** or leads to cyclohexene and **3** by a second H-atom transfer (Scheme 4). Reaction with *tert*-butanol occurs quite analogously to furnish **3** and **5** (Scheme 3); the primary adduct, which is analogous to **4**, cyclises to form an imino ether (two epimers) which in turn is hydrolysed during work-up to form **5**. Reaction with solvent is only modestly higher (by a factor of roughly 3) if methanol is used in place of cyclohexane, but much higher if cyclopentene is used which on H-atom abstraction yields an allylically stabilised residue. (A complicated mixture of products was obtained with cyclopentene, which was not investigated.) Reaction with solvent thus represents a free

[1] Spherical symmetry around the quenched molecule, as assumed in Perrin's work, is not necessary. Rather, the quenching equation can as well be derived by integrating any infinitesimal elements of volume.



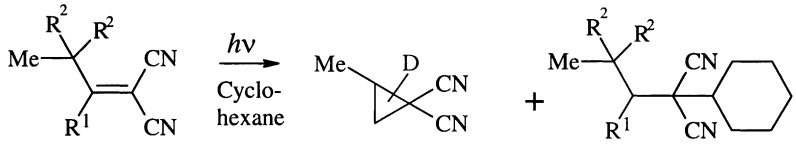
8

Scheme 4.

radical reactivity of the photoexcited DCNA chromophore; in case of a cationic reactivity, hydride abstraction would have been much more efficient with methanol than with cyclopentene, in contrast to observation. The isolation (in one case when atmospheric oxygen had not been excluded rigorously enough) of **8**, which is the trapping product of the cyclohexyl/alkyldicyanomethyl radical pair by atmospheric oxygen, more directly documents the radical mechanism. Since OCPR arises from cationic reactivity of C-2 [38], this divergent reactivity, cationic versus radical, suggests that the two reactions, OCPR and H-abstraction from solvent, are due to two different excited DCNA species. This is actually the case as is documented by the secondary H/D isotope effects for either reaction presented in Scheme 5. OCPR is found to be faster if the unsaturated C-2 atom, which becomes saturated in the first step, bears H rather than D. Accordingly, in the case of OCPR, the (C-2)-(H/D) bond had effectively higher force constants in the reactive species (when C-2 was unsaturated) than after C-2 became saturated. For the addition of cyclohexane (i.e. for the H-atom abstraction from cyclohexane), occurring in competition to OCPR, however, the reverse is observed. In the case of this reaction the (C-2)-(H/D) bond had effectively lower force constants in the reactive species (when C-2 was unsaturated) than after C-2 became saturated. The question remains as to the spin multiplicity of the hydrogen abstracting species. The presence of up to 0.17 M *E*-1,3-pentadiene (*t*-pip) which efficiently quenched the triplet state of **1a12** (vide supra) did not significantly change the ratio of the OCPR product **2b3** over the hydrogen adduct **3a12** both of which arise from **1a12**; this ratio decreased slightly from 42.7 ± 2.1 in the absence of *t*-pip to 37.0 ± 1.4 in the presence of 0.17 M *t*-pip, the decrease presumably being due to additional formation of **3a12** by facile hydrogen abstraction from the allylic position of *t*-pip (cf. cyclopentene, vide supra). In conclusion, not being quenched by *t*-pip, hydrogen abstraction is a singlet state reaction like OCPR.

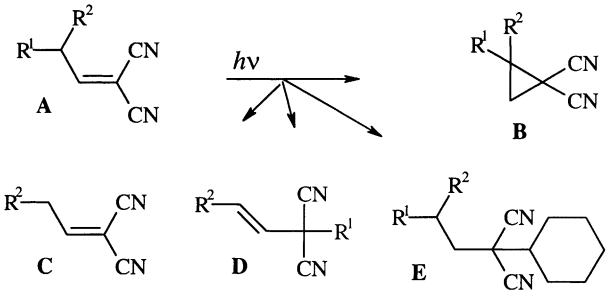
3.5. The 3,4-bond cleavage reaction

Scheme 6 displays the product distribution observed after direct irradiation of two DCNA (**1a4** and **1a7**) bearing



R^1	R^2	$k_{rel.}$	$k_{rel.}$
H	H	≡ 1.00	≡ 1.00
H	D	0.77 ± 0.08	1.03 ± 0.09
D	H	0.96 ± 0.08	1.36 ± 0.20
D	D	0.60 ± 0.04	1.18 ± 0.09

Scheme 5.



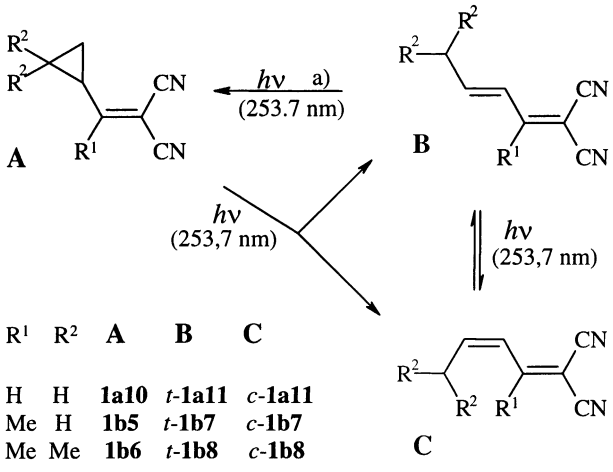
R^1	R^2	A	B	C	D
t-Bu	Me	**1a7**	**2a7**	**1a2**	**9**
t-Bu	H	**1a4**	**2a4**	**1a1**	**10**
Allyl	H	**1a5**	**2a5**	**1a1**	**11**

Quantum yields (extrapolated to zero conversion) for products obtained from irradiations of **A** at 253.7 nm:

R^1	R^2	sol.[a)]	$10^2\Phi_B$	$10^2\Phi_C$	$10^2\Phi_D$	$10^2\Phi_{C+D}$	$10^2\Phi_E$
t-Bu	Me	Cyh	4.6	3.8	3.8	7.6 (9.9[b)])	0.04
t-Bu	H	Cyh	3.4	4.6	1.0	5.6 (7.4[b)])	0.2
"	"	t-B	3.6	4.3	0.9	5.2	
Allyl	"	Cyh	4.3	0.03	8.1	8.1	
"	"	t-B	4.9	0.4	9.6	10.0	
"	"	AN	2.9	0.13	9.9	10.0	

[a)] solvent: Cyh = cyclohexane; t-B = tert-butanol; AN = acetonitrile
[b)] including various unidentified products

Scheme 6.



R^1	R^2	A	B	C
H	H	**1a10**	*t*-**1a11**	*c*-**1a11**
Me	H	**1b5**	*t*-**1b7**	*c*-**1b7**
Me	Me	**1b6**	*t*-**1b8**	*c*-**1b8**

	$10^2\Phi_{(B+C)}$
1a10	24 ± 4
1b5	7.3

a) Only observed with R^2 = Me (g.l.c. analysis; photostationary state **1b6** : *t*-**1b8** : *c*-**1b8** = 5.8±0.1 : 79.4±0.3 : 14.8±0.2, established both from pure **1b6** and from pure *t*-**1b8**, while accompanyied by further irreversible changes)

Scheme 7.

tert-butyl groups on C-3. **B** and **E** are the expected OCPR and cyclohexane addition products. Products **C** and **D**, however, which are formed in combined chemical yields exceeding those of **B**, are unique among all "lone" DCNA investigated in the present work. They arose from a cleavage of the bond between C-3 and the *tert*-butyl group. Of all "lone" DCNA investigated, **1a4** and **1a7** were the only ones bearing a tertiary alkyl group on C-3. Compound **1a3**, which differs from **1a4** in that it bears an isopropyl instead of a *tert*-butyl group, did not form products **C** and **D** in any significant amount.

The "3,4-bond cleavage" as exhibited by **1a4** and **1a7** is not new in the field of DCNA. It had been found before, particularly by the group of Cookson [4–8]. In the hands of these workers, the residues on C-3 that were cleaved off were of the allyl and benzyl type throughout. The present study shows that *tert*-butyl can do as well. For the sake of comparison, we have included **1a5**, which is the simplest 3-allyl-substituted DCNA and which so far had not been studied, in our study. The results obtained with this compound, which are also included in Scheme 6, show that **1a5** behaves quite similar to **1a4** and **1a7**. Compound **1a5** also gives the OCPR product, **2a5**, in competition to 3,4-bond cleavage. This contrasts with the results obtained in the Cookson group, where only 3,4-bond cleavage but no OCPR had been observed. The reason for this is that these workers had investigated only DCNA belonging to structure types **4** and **5** [38] and, therefore, exhibiting particularly low OCPR quantum yields [38].

There is another type of "lone" DCNA that exhibit 3,4-bond cleavage as their almost sole primary photoreaction on direct irradiation, even though they do not form products of type **C** and **D**, namely, 2-cyclopropyl-DCNA (Scheme 7).

Sharma in the group of Cookson had shown 3,4-bond cleavage to be a singlet-state reaction since it occurred on direct irradiation whereas on triplet sensitisation an entirely different reaction occurred, namely, crossed intramolecular [2 + 2] cycloaddition [8]. The quantum yields for 3,4-bond cleavage observed in the present work (Schemes 6 and 7), which are much higher than the quantum yield observed for **1a12** triplet formation (vide supra), bear out this conclusion.

3.6. The reactive state

The lowest singlet $\pi\pi^*$ state, which is the one we activate by irradiation, can accommodate an entire family of species, not necessarily energy minima, that differ in their angles of twist about the formal C=C double bond. As pointed out by Salem on grounds of quantum mechanical calculations [54], the perpendicular geometry (twist angle: 90°) of an olefin in its lowest excited singlet state, which generally is also its energetically most stable geometry, will be fully polarised into a carbanion/carbonium ion pair in the presence of even modest asymmetry, let alone the strong asymmetry caused

by the two polar cyano groups. With zero or modest twist angles, by contrast, there will be no polarisation. Since all three reactions that we observe, namely, OCPR, hydrogen abstraction, and 3,4-bond cleavage, are excited singlet state reactions (vide supra), all three of them must occur from the lowest excited singlet state ($\pi\pi^*$) since this is the one that we activate by irradiation. We can therefore ascribe OCPR (which is due to cationic reactivity at C-2 [38]) to the perpendicular (and presumably energetically most stable) geometry of this state and the H-abstraction (due to radical reactivity at C-2, vide supra) to geometries of lower (presumably $<80^\circ$) twist. These latter geometries appear to represent either no or only very flat energy minima, as is suggested by the DCNA being non-fluorescent. We cannot assign 3,4-bond cleavage to either cationic or radical reactivity at first. However, we observe that its quantum yields ($10^2\Phi_{\mathbf{C+D}}$ in Scheme 6) are surprisingly similar for **1a4**, **1a5**, and **1a7**, even though the driving force for 3,4-bond cleavage should be quite different for the three compounds. Thus, **1a7** in its most stable conformation [38] has the (C-3)-*tert*-butyl bond – which is to break – well-aligned with the (C-2)-π orbital, whereas **1a4** has it orthogonal; moreover, the additional methyl group in **1a7** should facilitate the bond cleavage. Obviously, 3,4-bond cleavage in all three cases, **1a4**, **1a5**, and **1a7**, scavenges some species encompassed by the lowest singlet $\pi\pi^*$ state, but it does not occur from other species also encompassed. We therefore suggest the following scenario consistent with all facts so far observed. The DCNA chromophore in its lowest electronically excited singlet state is at first formed in a manifold of vibrationally excited states that can be broadly classified in two groups, namely, those species which more strongly vibrate about the 90° (perpendicular) twist angle and, therefore, periodically achieve moderately twisted geometries, and those species less strongly vibrating in this way and, therefore, remaining close to the perpendicular conformation all time. In the absence of a propensity for 3,4-bond cleavage, part of the former group will undergo H-abstraction while residing at moderately twisted geometries whereas the rest of the former group will relax irreversibly to join the latter group which besides decay can only undergo OCPR. In the presence of efficient 3,4-bond cleavage, most species of the former group will be scavenged by the 3,4-bond cleavage, while residing at moderately twisted geometries, before they can relax or undergo H-abstraction. Accordingly, we observe an OCPR quantum yield for **1a7** (0.046) that is significantly reduced by the competing 3,4-bond cleavage as compared to **1a6**, **1a8**, and **1a9** (0.077–0.103 [38]; for **1a4** and **1a5**, the situation is similar. (Note that the true 3,4-bond cleavage quantum yield will be higher than the observed one since part of the cleaved molecules will recombine to form starting material.) H-abstraction quantum yields are even more strongly reduced, as expected. A corollary of this scenario is that 3,4-bond cleavage represents radical reactivity of C-2. As suggested by the very fast and efficient bond cleavage undergone by cyclopropylmethyl cations [55,56] and radicals [57], 3,4-bond cleavage in the case of the cyclopropyl DCNA can occur efficiently both via ionic and radical reactivity and hence, from any twist geometry. It is so efficient that it eliminates all competing reactions.

4. Conclusion

Three important reactions occur from the lowest excited singlet state (a $\pi\pi^*$ state) of DCNA devoid of further unsaturation and heteroatoms (“lone” DCNA); namely, OCPR, hydrogen abstraction from solvent, and 3,4-bond cleavage. The first one represents cationic and the other two represent radical reactivity of the C-2 of the excited DCNA molecule. Further minor reaction products are branched off the OCPR reaction path. It is suggested that OCPR occurs from the perpendicular geometry of the excited double bond whereas H-abstraction and 3,4-bond cleavage occur from geometries intermediate between planar and perpendicular which arise by vibration about the perpendicular geometry. Only part of the photoexcited DCNA molecules are born with such vibration being sufficiently excited. The 3,4-bond cleavage can scavenge these vibrating molecules before they relax to the perpendicular geometry.

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Appendix A. Determinations of molecular structures

A.1. General

The structures of two new compounds were determined by X-ray crystallography. A few new compounds were prepared by independent syntheses which confirmed their identification. The structures of most new compounds were unambiguously determined solely by NMR spectroscopy. This was possible due to the availability of 400 MHz-^{1}H NMR including spin decoupling and NOE experiments where appropriate, of 100 MHz-^{13}C NMR (gated, BB-decoupled, and DEPT), and of C-, H-correlation spectroscopy.

A.2. 1,1-Dicyano-cyclopropanes (2)

The preparation, by routes different from OCPR, of the following 1,1-dicyano-cyclopropanes encountered in the present work has been described in the literature: **2a1** [58], **2a2** [59], **2a3** [60], **2a4** [61], **2a6** [39,58], **2b1**–**2b2** [58], **2b3** [39], **2b5** [39,58], and **2b6**–**2b8** [40]. For rigorous identification of OCPR products, we repeated these preparations. In addition, the following 1,1-dicyano-cyclopropanes were synthesised by us. A mixture of **2a8** and **2a9** was prepared from 1-methylene-2-methyl-cyclohexane [41,42] according to the method of Boldt [39,40] and furnished **2a8** on crystallisation. Another mixture of **2a8** and **2a9** was prepared according to the method of Annen [43] from **1b12** and was separated into pure **2a8** and **2a9**. Then **2b10** was prepared from 1,4-dimethyl-cyclohexene [44] according to the method of Boldt [39,40]. The molecular structures of **2b13** and **2b14** were determined by X-ray crystallography. The molecular constitutions of the 10 other 1,1-dicyano-cylopropanes encountered in the present work could be unambiguously determined by NMR spectroscopy. Characteristically high values (ca. 160 Hz) for the $^1J_{C,H}$ and characteristically low absolute values (5–6 Hz) for the geminal $J_{H,H}$ constants on saturated C-atoms were diagnostic for cyclopropane rings. Furthermore, the dicyano-substituted quaternary cyclopropane C-atoms were found to exhibit δ-values depending characteristically on the number of alkyl groups on the cyclopropane ring, namely, -1.8, 4.4, 9.2 ± 0.5, 10.0 ± 0.5, 14.4 ± 0.7, and 19.8 for unsubstituted, mono-, 2,3-di-, 2,2-di-, tri-, and tetra-alkylated 1,1-dicyano-cyclopropane, respectively. Both **2a8** and **2a9** possess chair conformations of their cyclohexane rings with axial methyl groups as follows from an analysis of their $J_{H,H}$ patterns and ^{1}H,^{1}H-NOE experiments. On this basis, the assignment to structures **2a8** and **2a9** was possible by means of the characteristically high *trans*-$^3J_{C,H}$ values between the cyclopropane C-atom that is axial on the cyclohexane ring and the axial H-atom of the neighbouring cyclohexane methylene group. Of the cyclopropane C-atoms, only $\underline{C}(CN)_2$ in **2a8** and $\underline{C}H_2$ in **2a9** exhibited such high values, namely, 10.6 and 8.3 Hz, respectively. The gauche $^3J_{rmC,H}$ values of these C-atoms to the two equatorial cyclohexane hydrogen atoms were 2×3.5 and 2×2.7 Hz, respectively. The assignment to the epimeric structures **2b1** and **2b2** follows from the presence of two and of one ^{13}CN resonances, respectively, in the NMR spectra of the two compounds. The conformation (half-chair) and relative configurations of the closely related compounds **2b9**–**2b11** and **2b16**–**2b17** follow from the analysis of their $J_{H,H}$ patterns and from ^{1}H,^{1}H-NOE experiments. The relative configuration of **2b12** follows per exclusionem from that of **2b13** (vide supra). The structure of **2b15** was assigned to a by-product formed with the expected quantum yield and appearing in the analytic gas chromatograms of the crude photolysis product obtained from **1b12**; the other observed by-products were due to reaction of **1b12** with solvent. We could not reproduce an independent synthesis of **2b18** reported in the literature [40]; the structure of **2b18** follows from its NMR data which reveal the twofold symmetry of the compound.

A.3. Hydrogenation products 3

We prepared **3a2** [62], **3a6** [63], **3b2** [64], **3b9** [20], **3b11** [64], and **3b12** (1:1 mixture of both epimers) by catalytic hydrogenation (Pd/C, ethanol, discontinued after uptake of 1 mol hydrogen, purification by distillation) of the respective DCNA. The compounds were identified on basis of their ^{1}H NMR spectra; the ^{1}H resonances between $\delta = 3.5$ and 4.0 were characteristic; clean triplets in the first two, and clean doublets in the other cases. These independent preparations allowed the identification and quantification of these compounds in the irradiated mixtures by capillary g.l.c. Both epimers of **3b17** were isolated besides the OCPR products after irradiation of **1b17** in *tert*-butanol and were identified on basis of their NMR spectra; the $J_{H,H}$ patterns allowed the assignments of the relative configurations.

A.4. Cyclohexane adducts 4 and tert-butanol adducts 5

The cyclohexane adducts **4a1**, **4a4**, **4a6**, **4b9**, **4b11**, **4b12**, **4b18**, **4b19**, and **4b20** were isolated after irradiation of respective DCNA in cyclohexane. Their constitutions followed from their NMR data and demonstrated the regioselectivity of the cyclohexane addition. (In all cases, the carbon atom bearing the two cyano groups was quaternary according to NMR.) In addition, **4b11** was independently synthesised (from malononitrile with two moles of bromocyclohexane). All other cyclohexane adducts were identified in the capillary gas chromatograms since they appeared at characteristic time delays after the OCPR products and only after irradiation in cyclohexane but not in any other solvent including *n*-hexane. Two cyclohexane adducts were observed in those cases were two epimers of **4** were possible, and one single one was observed in the other cases.

The constitutions of the *tert*-butanol adducts **5b17** and **5b18** (two epimers in each case) followed from their NMR data and C, H, N analysis.

A.5. Miscellaneous products

Compound **6** was synthesised from malononitrile and methallyl chloride [65] and identified on account of its ^{1}H NMR spectrum. The constitutions of **8**–**11** were completely elucidated by ^{1}H and ^{13}C NMR spectroscopy. In addition, **11** was synthesised from **1a1** and allyl bromide. The molecular weight of **8** was established by mass spectrometry.

A.6. NMR data

1a4: ^{1}H NMR ($CDCl_3$): $\delta = 1.00$ (s, 9H), 2.47 (d, $J = 8.0$ Hz, 2H), 7.43 (t, $J = 2 \times 8.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 29.0$ (CH_3), 32.8 (C), 46.4 (CH_2), 90.5 (C), 110.5 (CN), 112.0 (CN), 168.0 (CH).

1a7: ^{1}H NMR ($CDCl_3$): $\delta = 0.94$ (s, 9H), 1.08 (d, $J = 6.8$ Hz, 3H), 2.67 (dq, $J = 11.4$, 3×6.8 Hz, 1H), 7.24 (d, $J = 11.4$ Hz, 1H).

1a8: ^{1}H NMR ($CDCl_3$): $\delta = 0.90$ (d, $J = 7.1$ Hz, 3H), 1.23–1.78 (m, 8H), 1.92 (dqt, $J = 9.5$, 3×7.1, 2×4.0 Hz, 1H), 2.98 (dq, $J = 11.2$, 3×4.6 Hz, 1H), 7.50 (d, $J = 11.2$ Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 18.0$, 22.1, 23.7, 29.2, 30.4, 34.4, 44.5, 89.2, 110.6, 112.3, 172.4.

1a9: ^{1}H NMR ($CDCl_3$): $\delta = 0.89$ (d, $J = 6.5$ Hz, 3H), 1.05 (qd, 3×12.0, 3.0 Hz, 1H), 1.18–1.48 (m, 4H), 1.63–2.05 (m, 4H), 2.37 (qd, 3×11.0, 4.0 Hz, 1H), 7.20 (d, $J = 11.0$ Hz, 1H).

1b4: ^{1}H NMR ($CDCl_3$): $\delta = 1.1$–1.5 (m, 5H), 1.5–2.0 (m, 5H), 2.22 (s, 3H), 2.90 (m, 1H).

1b7: ^{1}H NMR ($CDCl_3$): $\delta = 2.00$ (d, $J = 5.8$ Hz, 3H), 2.30 (bs, 3H), 6.68 (dqq, $J = 15.4$, 3×5.8, 3×0.8 Hz, 1H), 6.74 (d, $J = 15.4$ Hz, 1H).

1b8: ^{1}H NMR ($CDCl_3$): $\delta = 1.10$ (d, $J = 7.0$ Hz, 6H), 2.33 (s, 3H), 2.50 (m, 1H), 6.67 (m, 2H).

1b19: ^{1}H NMR ($CDCl_3$): $\delta = 1.56$ (m, 2H), 1.90 (m, 4H), 2.0–2.2 (m, 6H), 3.19 (bs, 2H).

2a2: ^{1}H NMR ($CDCl_3$): $\delta = 1.40$ (d, $J = 6.3$ Hz, 3H), 1.47 (dd, $J = 8.2$, 5.7 Hz, 1H, 3-H *cis* to methyl), 1.90 (dd, $J = 9.0$, 5.7 Hz, 3-H *trans* to methyl), 2.05 (ddq, $J = 9.0$, 8.2, 3×6.3 Hz, 2-H). ^{13}C NMR ($CDCl_3$): $\delta = 4.4$ (s), 14.7 (q, $J = 3 \times 130$ Hz), 25.6 (t, $J = 2 \times 168$ Hz), 26.0 (d, $J = 167$ Hz), 113.7 (s), 115.5 (s).

2a3: ^{1}H NMR (CD_3COCD_3): $\delta = 1.13$ (d, $J = 6.6$ Hz, 3H), 1.19 (d, $J = 6.6$ Hz, 3H), 1.34 (dsept, $J = 9.8$, 6×6.6 Hz, 1H), 1.80 (dd, $J = 7.9$, 5.3 Hz, 1H), 2.00 (ddd, $J = 9.8$, 9.0, 7.9 Hz, 1H), 2.08 (dd, $J = 9.0$, 5.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 3.4$ (s), 20.75 (q, $J = 3 \times 126$ Hz), 20.80 (q, $J = 3 \times 126$ Hz), 24.2 (t, $J = 2 \times 168.1$ Hz), 30.7 (d, $J = 125.3$ Hz), 38.1 (d, $J = 164.7$ Hz), 113.8 (s), 115.3 (s).

2a4: ^{1}H NMR (C_6D_6): $\delta = 0.54$ (s, 9H), 0.70 (dd, $J = 10.0$, 6.5 Hz, 1H), 0.74 (dd, $J = 9.0$, 6.5 Hz, 1H), 1.03 (dd, $J = 10.0$, 9.0 Hz, 1H).

2a7: ^{1}H NMR ($CDCl_3$): $\delta = 1.11$ (s, 9H), 1.40 (s, 3H), 1.55 (d, $J = 6.0$ Hz, 1H), 2.02 (d, $J = 6.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 8.2$ (s), 19.6 (q, $J = 3 \times 128.6$ Hz), 25.7 (q, $J = 3 \times 126$ Hz), 29.0 (dd, $J = 165.7$, 167 Hz), 33.1 (s), 43.2 (s), 115.3 (s), 115.5 (s).

2a8: (3*R**4*S**-4-methyl-spiro[2.5] octane-1,1-dicarbonitrile). ^{1}H NMR ($CDCl_3$): $\delta = 1.08$ (d, $J = 7.1$ Hz, 3H, CH_3), 1.16 (dddt, $J = 14.7$, 3.5, 3.0, 2×1.5 Hz, 1H, 8-H_{eq}), 1.38 (tddd, $J = 2 \times 13.0$, 12.8, 4.0, 3.5 Hz, 1H, 7-H_{ax}), 1.49, 1.52 (2 m, 2H, 6-H), 1.52, 1.54 (AB-system, $J = 5.6$ Hz, 2H, 2-H), 1.55 (m, 1H, 4-H_{eq}), 1.60 (m, 2H, 5-H), 1.76 (ddq, $J = 12.8$, 3.9, 3×3.0 Hz, 1H, 7-H_{eq}), 2.01 (ddd, $J = 14.7$, 13.0, 3.9 Hz, 1H, 8-H_{ax}). ^{1}H,^{1}H-spin-decouplings by irradiations at $\delta = 1.16$, 1.76, 2.01. Strong ^{1}H,^{1}H-NOE enhancement: $\delta = 1.08$–2.01. ^{13}C NMR ($CDCl_3$): $\delta = 9.9$ (dt, $J = 10.6$, 2×3.5 Hz, C-1), 15.6 (qdt, $J = 3 \times 126.1$, 6.8, 2×4.1 Hz, CH_3), 18.3 (bt, $J = 2 \times 128$ Hz, C-6), 23.9 (bt, $J = 2 \times 129$ Hz, C-7), 26.8 (bt, $J = 2 \times 130$ Hz, C-8), 29.3 (bt, $J = 2 \times 130$ Hz, C-5), 30.3 (bt, $J = 2 \times 166.8$ Hz, C-2), 33.5 (bd, $J = 129.4$ Hz, C-4), 41.4 (bs, C-3), 114.3 (t, $J = 2 \times 4.4$ Hz, CN), 114.4 (t, $J = 2 \times 4.4$ Hz, CN).

2a9: (3*S**4*S**-4-methyl-spiro[2.5]octane-1,1-dicarbonitrile). ^{1}H NMR ($CDCl_3$): $\delta = 1.15$ (dddd, $J = 13.6$, 3.8, 3.0, 1.5 Hz, 1H, 8-H_{eq}), 1.21 (d, $J = 7.0$ Hz, 3H, CH_3), 1.34 (qdd, $J = 3 \times 13.0$, 7.0, 3.8 Hz, 1H, 7-H_{ax}), 1.56 (m, 3H, 4-H_{eq}, 6-H), 1.59 (m, 1H, 5-H_{ax}), 1.64 (s, 2H, 2-H), 1.69 (m, 1H, 5-H_{eq}), 1.89 (ddtdd, $J = 13.0$, 4.0, 2×3.5, 3.0, 1.5 Hz, 1H, 7-H_{eq}), 2.10 (ddd, $J = 13.6$, 13.0, 4.0 Hz, 1H, 8-H_{ax}). ^{1}H,^{1}H-spin-decouplings by irradiations at $\delta = 1.15$, 1.34, 1.89, 2.10. Strong ^{1}H,^{1}H-NOE enhancement: $\delta = 1.21$–2.10. ^{13}C NMR ($CDCl_3$): $\delta = 9.8$ (bs, C-1), 15.0 (qdt, $J = 3 \times 126.1$, 6.3, 2×3.3 Hz, CH_3), 19.3 (bt, $J = 2 \times 127$ Hz, C-6), 25.4 (tdt, $J = 2 \times 125.3$, 6.1, 2×3.0 Hz, C-7), 27.8 (bt, $J = 2 \times 131.4$ Hz, C-8), 31.3 (tsext, 2×128.4, 5×4.1 Hz, C-5), 32.0 (tdt, $J = 2 \times 166.8$, 8.3, 2×2.7 Hz, C-2), 35.2 (bd, $J = 129.7$ Hz, C-4), 42.1 (bs, C-3), 114.3 (t, $J = 2 \times 4.3$ Hz, CN), 114.4 (t, $J = 2 \times 4.4$ Hz, CN).

2b1: ^{1}H NMR ($CDCl_3$): $\delta = 1.27$ (m, 6H), 2.09 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 8.7$ (q, $J = 3 \times 129$ Hz), 9.2 (s), 29.8 (d, $J = 166$ Hz), 112.4 (s), 115.9 (s).

2b2: ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (m, 6H), 1.69 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 10.1$ (s), 14.6 (q, $J = 3 \times 129$ Hz), 33.3 (d, $J = 165$ Hz), 114.0 (s).

2b4: ^{1}H NMR ($CDCl_3$): $\delta = 1.34$ (d, $J = 6.5$ Hz, 3H), 1.65 (mc, 10H), 1.84 (q, $J = 3 \times 6.5$ Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 9.5$ (q, $J = 3 \times 128$ Hz), 14.2 (s), 24.5, 24.7, 25.2, 26.9, 34.4 (each a t, $J = 2 \times 129$ Hz), 36.8 (d, $J = 164$ Hz), 41.3 (s), 113.2 (s), 115.0 (s).

2b9: (1*S**,4*R**,6*R**-1,4-dimethyl-bicyclo[4.1.0]heptane-7,7-dicarbonitrile; half-chair conformation with equatorial 4-methyl): ^{1}H NMR ($CDCl_3$): $\delta = 0.84$ (d, $J = 6$ Hz, 3H, 4-CH_3), 1.10 (dddd, $J = 14.0$, 12.5, 12.0, 5.8 Hz, 1H, 3-H_{ax}), 1.14 (ddd, $J = 15.0$, 12.0, 2.8 Hz, 1H, 5-H_{ax}), 1.27 (tqdd, $J = 2 \times 12.0$, 3×6.0, 4.0, 2.5 Hz, 1H, 4-H_{ax}), 1.38 (s, 3H, 1-CH_3), 1.43 (dddd, $J = 14.0$, 7.1, 2.5, 1.5 Hz, 1H, 3-H_{eq}), 1.82 (ddd, $J = 15.5$, 12.5, 7.1 Hz, 1H, 2-H_{ax}), 1.97 (dd, $J = 9.7$, 2.8 Hz, 1H, 6-H), 2.13 (ddd, $J = 15.5$, 5.8, 1.5 Hz, 1H, 2-H_{eq}), 2.22 (ddd, $J = 15.0$, 9.7,4.0 Hz, 1H, 5-H_{eq}). Strong ^{1}H,^{1}H-NOE enhancements: $\delta = 1.38$–1.82, 1.38–1.97. ^{13}C NMR ($CDCl_3$): $\delta = 14.5$ (bs, C-7), 20.9 (q, $J = 3 \times 125.3$ Hz, 4-CH_3), 24.5 (qt, $J = 3 \times 128.5$, 2×4.5 Hz, 1-CH_3), 27.1 (bd, $J = 128$ Hz, C-4), 27.7 (bt, $J = 2 \times 127$ Hz, C-2), 28.2 (bt, $J = 2 \times 126$ Hz, C-3), 28.5 (bt, $J = 2 \times 128$ Hz, C-5), 33.6 (bs, C-1), 37.2 (bd, $J = 166$ Hz, C-6), 113.5 (d, $J = 2.4$ Hz, CN), 115.0 (d, $J = 5.7$ Hz, CN).

2b10: (1*S**,4*S**,6*R**-1,4-dimethyl-bicyclo[4.1.0]heptane-7,7-dicarbonitrile; half-chair conformation with equatorial 4-methyl): ^{1}H NMR ($CDCl_3$): δ = 0.88 (d, J = 6 Hz, 3H, 4-CH_3), 0.94 (dtd, J = 13.3, 2 × 11.3, 5.2 Hz, 1H, 3-H_{ax}), 1.47 (s, 3H, 1-CH_3), 1.50 (m, 1H, 3-H_{eq}), 1.57 (m, 2H, 4-H_{ax}, 5-H_{ax}), 1.83 (ddd, J = 15.6, 11.3, 4.9 Hz, 1H, 2-H_{ax}), 1.90 (dd, J = 6.2, 1.5 Hz, 1H, 6-H), 1.99 (ddd, J = 15.6, 5.2, 4.0 Hz, 1H, 2-H_{eq}), 2.09 (m, 1H, 5-H_{eq}). Strong ^{1}H,^{1}H-NOE enhancements: δ = 1.47–1.90, 1.47–1.99. ^{1}H NMR (C_6D_6): δ = 0.27 (dddd, J = 13.2, 11.7, 11.0, 5.3 Hz, 1H, 3-H_{ax}), 0.46 (d, J=6.5 Hz, 3H, 4-CH_3), 0.76 (ddd, J = 15.2, 10.0, 7.0 Hz, 1H, 5-H_{ax}), 0.81 (s, 3H, 1-CH_3), 0.96 (ddddd, J = 13.2, 5.0, 4.0, 3.0, 1.0 Hz, 1H, 3-H_{eq}), 0.98 (dd, J = 7.0, 1.5 Hz, 1H, 6-H), 1.20 (ddd, J = 15.5, 5.3, 4.0 Hz, 1H, 2-H_{eq}), 1.28 (ddqdd, J = 11.0, 10.0, 3 × 6.5, 5.6, 3.0 Hz, 1H, 4-H_{ax}), 1.38 (ddd, J = 15.5, 11.7, 5.0 Hz, 1H, 2-H_{ax}), 1.46 (dddd, J = 15.2, 5.6, 1.5, 1.0 Hz, 1H, 5-H_{eq}). ^{13}C NMR ($CDCl_3$): δ = 14.7 (bs, C-7), 21.6 (bq, J = 3 × 125 Hz, 4-CH_3), 24.6 (qt, J = 3 × 128.8, 2 × 5.0 Hz, 1-CH_3), 25.1 (bd, J = 129 Hz, C-4), 27.3 (tq, J = 2 × 129, 3 × 3.0 Hz, C-2), 28.4 (tquint, J = 2 × 129.7, 4 × 4.8 Hz, C-5), 28.9 (tquint, J = 2 × 127.6, 4 × 4.0 Hz, C-3), 34.5 (bs, C-1), 37.7 (bd, J = 163.8 Hz, C-6), 114.1 (d, J = 3.0 Hz, CN), 115.1 (d, J = 5.8 Hz, CN).

2b11: (1*S**,3*S**,6*R**-3-(*tert*-butyl)-bicyclo[4.1.0]heptane-7,7-dicarbonitrile; half-chair conformation with equatorial 3-*tert*-butyl): ^{1}H NMR ($CDCl_3$): δ = 0.84 (s, 9H, 3-*tert*-butyl), 0.98 (tdd, J = 2 × 12.5, 4.3, 2.5 Hz, 1H, 3-H_{ax}), 1,12 (dtd, J = 14.0, 2 × 12.4, 5.6 Hz, 1H, 4-H_{ax}), 1.34 (ddd, J = 15.0, 12.5, 2.0 Hz, 1H, 2-H_{ax}), 1.60 (ddtd, J = 14.0, 6.8, 2 × 2.5, 2.1 Hz, 1H, 4-H_{eq}), 2.03 (dddd, J = 15.2, 12.3, 6.8, 6.2 Hz, 1H, 5-H_{ax}), 2.10 (ddd, J = 9.0, 6.2,1.0 Hz, 1H, 6-H), 2.24 (dddd, J = 15.2, 5.6, 2.1, 1.0 Hz, 1H, 5-H_{eq}), 2.30 (ddd, J = 9.8, 9.0, 2.0 Hz, 1H, 1-H), 2.35 (dddd, J = 15.0, 9.8, 4.3, 2.5 Hz, 1H, 2-H_{eq}). ^{1}H NMR (C_6D_6): δ = 0.26 (dddd, J = 13.0, 12.4, 4.6, 2.8 Hz, 1H, 3-H_{ax}), 0.60 (s, 9H, 3-*tert*-butyl), 0.77 (ddd, J = 15.0, 13.0, 2.8 Hz, 1H, 2-H_{ax}), 0.86 (dddd, J = 14.0, 12.4, 12.0, 5.6 Hz, 1H, 4-H_{ax}), 1.00 (m, 1H, 4-H_{eq}), 1.08 (m, 1H, 6-H), 1.09 (m, 1H, 5-H_{ax}), 1.24 (ddd, J = 9.8, 9.0, 2.8 Hz, 1H, 1-H), 1.44 (ddd, J = 15.0, 9.8, 4.6 Hz, 1H, 2-H_{eq}), 1.47 (m, 1H, 5-H_{eq}). ^{13}C NMR ($CDCl_3$): δ = 8.9 (C-7), 20.5 (C-4), 21.1 (C-2), 21.2 (C-5), 27.1 (3CH_3), 29.6 (C-6), 30.5 (C-1), 32.2 (C-3′), 42.6 (C-3), 113.4 (CN), 116.3 (CN).

2b12: ^{1}H NMR ($CDCl_3$): δ = 1.26 (dtdd, J = 15.0, 2 × 13.0, 7.0, 4.0 Hz, 1H), 1.48–1.94 (m, 13H), 2.09 (bd, J = 9.5 Hz, 1H), 2.31 (dddd, J = 15.0, 9.5, 7.0, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ = 13.3 (s), 20.1, 21.3, 25.0 (each a t, J = 2 × 130 Hz), 25.7, 26.3, 31.2, 36.1 (each a t, J = 2 × 126 Hz), 36.7 (d, J = 168 Hz), 39.4 (d, J = 126 Hz), 43.6 (s), 114.7 (s), 115.8 (s).

2b13: ^{1}H NMR ($CDCl_3$): δ = 1.20 (dq, J = 15.0, 3 × 6.0 Hz, 1H), 1.30–1.54 (m, 5H), 1.60 (dd, J = 15.0, 6.0 Hz, 1H), 1.66–1.90 (m, 6H), 1.95 (dd, J = 8.5, 2.0 Hz, 1H), 1.96 (m, 1H), 2.18 (ddt, J = 14.5, 8.5, 2 × 6.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ = 15.3 (s), 17.1, 20.1, 22.6, 22.7, 26.7, 30.1 (each a t, J = 127 Hz), 31.7 (d, J = 130 Hz), 33.1 (t, 2 × 127 Hz), 37.3 (d, J = 165 Hz), 39.8 (s), 114.3 (s), 115.2 (s).

2b14: ^{1}H NMR ($CDCl_3$): δ = 0.91 (tdd, J = 2 × 13.0, 11.0, 3.0 Hz, 1 methylene-H), 1.32 (qdd, J = 3 × 13.0, 6.0, 4.0 Hz, 1 methylene-H), 1.45–2.20 (m, 12H; 10 methylene-H, 1 methine-H at 2.01, 1 cyclopropyl-methine-H at 2.07). ^{13}C NMR ($CDCl_3$): δ = 13.8 (s), 19.0, 20.2, 25.0, 28.2, 34.7, 35.7 (each a t, J = 2 × 128 Hz), 35.8 (d, J = 162 Hz), 37.2 (d, J = 133.2 Hz), 44.5 (s), 113.9 (s), 115.0 (s).

2b16: (1*S**, 3*R**, 6*R**-3-(1,1-dimethylethyl)-bicyclo[4.1.0]heptane-7,7-dicarbonitrile; half-chair conformation with equatorial 3-*tert*-butyl): ^{1}H NMR ($CDCl_3$): δ = 0.81 (s, 9H, *tert*-butyl), 0.82 (m, 1H, 4-H_{ax}), 1.20 (tdd, J = 2 × 12.2, 5.5, 2.4 Hz, 1H, 3-H_{ax}), 1.53 (dddd, J = 15.3, 13.4, 4.5, 3.0 Hz, 1H, 5-H_{ax}), 1.59 (dddd, J = 12.7, 4.5, 2.4, 2.0 Hz, 1H, 4-H_{eq}), 1.71 (ddd, J = 15.3, 12.2, 6.3 Hz, 1H, 2-H_{ax}), 2.14 (ddd, J = 15.3, 5.5, 1.0 Hz, 1H, 2-H_{eq}), 2.23 (ddd, J = 9.3, 6.3, 3.0 Hz, 1H, 1-H), 2.27 (ddd, J = 9.3, 9.1, 3.0 Hz, 1H, 6-H), 2.40 (dddd, J = 15.3, 9.1, 4.5, 2.0 Hz, 1H, 5-H_{eq}). ^{13}C NMR ($CDCl_3$): δ = 9.5 (C-7), 21.0 (C-5), 21.4 (C-2), 22.6 (C-4), 26.8 (3CH_3), 30.0 (C-6), 31.5 (C-1), 32.6 (C-3′), 40.9 (C-3), 113.4 (CN), 116.3 (CN).

2b17: ^{1}H NMR ($CDCl_3$): δ = 1.17–1.75 (m, 11H), 1.88 (ddt, J = 15.5, 7.0, 2 × 6.0 Hz, 1H), 1.94 (dd, J = 10.0, 2.6 Hz, 1H), 2.01 (m, 1H), 2.12 (ddd, J = 15.5, 9.0, 7.0 Hz, 1H), 2.25 (dd, J = 10.0, 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ = 8.8 (s), 16.5, 22.9, 24.1, 24.2, 27.8 (each a t, J = 2 × 128 Hz), 29.4 (d, J = 170 Hz), 31.0 (t, J = 2 × 126 Hz), 31.0 (d, J = 128 Hz), 31.7 (d, J = 128 Hz), 34.0 (d, J = 170 Hz), 113.3 (s), 116.5 (s).

2b18: (1*S**, 2*S**, 4*R**, 5*R**-tricyclo[3.2.1.0^{2,4}]octane-3,3-dicarbonitrile): ^{1}H NMR ($CDCl_3$): δ = 1.61 (m, 3H, exo-6-H, exo-7-H, exo-8-H), 2.08 (bd, J = 9.1 Hz, 2H, endo-6-H, endo-7-H), 2.18 (bd, J = 8.7 Hz, 1H, endo-8-H), 2.51 (bs, 2H, 2-H, 4-H), 2.77 (bs, 1-H, 5-H). ^{1}H,^{1}H-NOE enhancement: 2-H, 4-H/endo-6-H, endo-7-H. ^{13}C NMR ($CDCl_3$): δ = 19.0 (C-3), 25.0 (C-6, C-7), 39.4 (C-1, C-5), 41.3 (C-2, C-4), 56.1 (C-8), 114.8 (CN), 115.5 (CN).

3b12: (1:1 mixture of both epimers): ^{1}H NMR ($CDCl_3$): δ = 0.94–0.97 (d, J = 7.0 Hz, 3H), 1.2–1.9 (m, 8H), 2.0–2.3 (m, 2H), 3.43–3.97 (d, J = 10.0–3.6 Hz, 1H).

3b17: (2-(*Trans*-4-(1,1-dimethyl-ethyl)-cyclohexyl)-malononitrile): ^{1}H NMR ($CDCl_3$): δ = 0.84 (s, 9H), 1.00 (tm, J = 2 × 11.0 Hz, 1H, 4′-H_{ax}), 1.07 (dddm, J = 12.8, 12.0, 11.0 Hz, 2H, 3′-H_{ax}), 1.28 (tdd, J = 2 × 12.8, 11.8, 3.6 Hz, 2H, 2′-H_{ax}), 1.90 (m, 2H, 3′-H_{eq}), 1.92 (tdt, J = 2 × 11.8, 5.9, 2 × 3.6 Hz, 1H, 1′-H_{ax}), 2.03 (m, 2H, 2′-H_{eq}), 3.54 (d, J = 5.9 Hz, 1H, 2-H). ^{13}C NMR ($CDCl_3$): δ = 26.3 (C-3′), 27.4 (CH_3), 29.2 (C-2), 30.3 (C-2′), 32.3 (C-4″), 39.4 (C-1′), 46.9 (C-4′), 112.0 (C-1, =CN).

3b17: (2-(*Cis*-4-(1,1-dimethyl-ethyl)-cyclohexyl)-malononitrile): ^{1}H NMR ($CDCl_3$): δ = 0.84 (s, 9H), 0.94 (m, 2H, 3′-H_{ax}), 1.06 (tt, J = 2 × 11.9, 2 × 3.9 Hz, 1H, 4′-H_{ax}), 1.70 (m, 4H, 2′-H_{ax}, 3′-H_{eq}), 2.04 (dddd, J = 13.6, 5.0,

3.0, 2.4 Hz, 2H, 2′-H_{eq}), 2.42 (dtt, $J = 11.5$, 2×4.3, 2×2.4 Hz, 1H, 1′-H), 3.80 (d, $J = 11.5$ Hz, 1H, 2-H). ^{13}C NMR ($CDCl_3$): $\delta = 21.1$ (C-3′), 24.4 (C-2), 27.3 (CH_3), 27.9 (C-2′), 32.5 (C-4″), 35.8 (C-1′), 47.5 (C-4′), 112.7 (C-1, =CN).

4a1: ^{1}H NMR ($CDCl_3$): $\delta = 1.18$ (m, 1H), 1.26 (t, $J = 2 \times 7.4$ Hz, 3H), 1.29 (m, 4H), 1.72 (m, 1H), 1.76 (m, 1H), 1.87 (m, 2H), 1.96 (q, $J = 3 \times 7.4$ Hz, 2H), 1.98 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 9.9$ (CH_3), 25.3 (CH_2), 25.5 ($2CH_2$), 28.4 ($2CH_2$), 28.5 (CH_2), 43.4 (CH), 44.3 (C), 115.1 (2CN).

4a4: ^{1}H NMR ($CDCl_3$): $\delta = 0.94$ (s, 9H), 1.28 (mc, 5H), 1. 53, 1.88 (A_2X_2-system, $J_{AB} = 13$ Hz, $J_{AB'} = 4.3$ Hz, $J_{AA} = J_{BB} = 12$ Hz, 4H), 1.7–1.9 (m, 4H), 2.00 (m, 2H).

4a6: ^{1}H NMR ($CDCl_3$): $\delta = 1.09$ (d, $J = 6.7$ Hz, 6H), 1.2–1.3 (m, 5H), 1.71 (m, 1H), 1.75 (m, 1H), 1.77 (d, $J = 6.7$ Hz, 2H), 1.87 (m, 2H), 2.00 (m, 2H), 2.06 (nonet, $J = 8 \times 6.7$ Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 22.8$ (CH_3), 25.4 (CH_2), 25.6 (CH_2), 26.6 (CH), 28.3 (CH_2), 41.5 (C), 43.0 (CH_2), 45.6 (CH), 115.5 (CN).

4b9: ^{1}H NMR ($CDCl_3$): $\delta = 1.07$ (d, $J = 6.9$ Hz, 3H), 1.49 (s, 9H), 1.2–1.3 (m, 3H), 1.30 (qd, $J = 3 \times 12.2$, 3.3 Hz, 1H), 1.46 (qd, $J = 3 \times 12.2$, 3.3 Hz, 1H), 1.70 (bd, $J = 10.0$ Hz, 1H), 1.81 (bd, $J = 10.5$ Hz, 1H), 1.85–1.91 (m, 3H), 1.94 (q, $J = 3 \times 6.9$ Hz, 1H), 2.11 (bd, $J = 12.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 12.5$ (CH_3), 25.5, 25.7, 25.8, 26.9 (each a CH_2), 28.6 (CH_3), 29.0 (CH_2), 34.5 (C), 43.7 (CH), 44.0 (C), 44.7 (CH), 115.3 (CN), 116.3 (CN).

4b11: ^{1}H NMR ($CDCl_3$): $\delta = 1.0$–1.55 (m, 10H), 1.55–2.2 (m, 12H). ^{13}C NMR ($CDCl_3$): $\delta = 25.5$, 25.7, 28.3 (each a CH_2), 40.4 (CH), 49.0 (C), 114.7 (CN).

4b12: ^{1}H NMR ($CDCl_3$): $\delta = 1.13$ (d, J=6.0 Hz, 3H), 1.1–2.5 (m, 21H).

4b18: ^{1}H NMR ($CDCl_3$): $\delta = 1.12$–1.35 (m, 6H), 1.37 (bs, 2H), 1.40–1.65 (m, 3H), 1.66–1.75 (m, 2H), 1.80–1.90 (m, 3H), 1.90–1.98 (m, 2H), 2.06 (bd, $J = 11$ Hz, 1H), 2.28–2.35 (m, 2H), 2.47 (bs, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 23.3$, 25.4, 25.7, 25.8, 28.3, 28.6, 29.2, 33.7 ($8CH_2$), 37.4 (CH), 40.2 (CH_2), 40.9, 43.9, 44.7 (3CH), 45.3 (C), 115.0, 115.2 (2CN).

4b19: ^{1}H NMR ($CDCl_3$): $\delta = 1.15$–1.38 (m, 5H), 1.57 (m, 3H), 1.70 (m, 4H), 1.8–2.02 (m, 10H), 2.10 (bs, 2H), 2.33 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 20.1$ (CH_2), 21.9 (CH_2), 24.0 ($2CH_2$), 25.5 (CH_2), 25.8 ($2CH_2$), 28.3 ($2CH_2$), 29.6 (2CH), 35.3 ($2CH_2$), 42.1 (CH), 44.7 (C), 44.9 (CH), 116.0 (2CN).

4b20: ^{1}H NMR ($CDCl_3$): $\delta = 1.13$–1.38 (m, 5H), 1.63 (bd, $J = 13.3$ Hz, 2H), 1.70–1.76 (m, 5H), 1.82–2.02 (m, 9H), 2.15 (m, 3H), 2.47 (bd, $J = 13.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 25.5$ (CH_2), 25.8 ($2CH_2$), 26.6 (CH), 27.8 (CH), 28.2 ($2CH_2$), 29.9 (2CH), 30.6 ($2CH_2$), 37.7 (CH_2), 40.3 ($2CH_2$), 42.7 (CH), 45.0 (C), 46.7 (CH), 116.1 (2CN).

5b17 (major stereoisomer): ^{1}H NMR ($CDCl_3$): $\delta = 0.84$ (s, 9H), 1.22 (td, $J = 3 \times 7.5$, 5 Hz, 1H), 1.47 (s, 3H), 1.49–1.58 (m, 6H), 1.58 (s, 3H), 1.72–1.9 (m, 2H), 2.14 (td, $J = 3 \times 9.2$, 6 Hz, 1H), 2.22, 2.50 (AB-system, $J = 13.7$ Hz, 2H). Minor stereoisomer, selected resonances: 0.82 (s, 9H), 1.46 (s, 3H), 1.57 (s, 3H), 2.18, 2.42 (AB-system, $J = 14.1$ Hz, 2H).

5b18 (major stereoisomer): ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ (bs, 2H), 1.42 (m, 1H), 1.46 (m, 1H), 1.47 (s, 3H), 1.56 (dd, $J = 13.5$, 3.8 Hz, 1H), 1.58 (m, 1H), 1.60 (s, 3H), 1.83 (m, 1H), 2.00 (ddt, $J = 13.5$, 11.2, 2×3.6 Hz, 1H), 2.12 (dt, 11.2, $J = 2 \times 3.7$ Hz, 1H), 2.25 (bt, $J = 2 \times 3.6$ Hz, 1H), 2.33 (bt, $J = 2 \times 3.6$ Hz, 1H), 2.22, 2.67 (AB-system, $J = 13.7$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 23.3$ (CH_2), 27.8 (CH_3), 28.7 (CH_2), 29.2 (CH_3), 33.8 (CH_2), 37.1 (CH), 39.96 (CH), 40.01 (CH_2), 45.2 (CH_2), 46.4 (C), 46.7 (CH), 83.3 (C), 118.5 (CN), 170.8 (COO).

6: ^{1}H NMR ($CDCl_3$): $\delta = 1.79$ (s, 3H), 2.67 (d, $J = 8.0$ Hz, 2H), 3.86 (t, $J = 2 \times 8.0$ Hz, 1H), 4.96 (bs, 1H), 5.07 (bs, 1H).

8: (1-Cyclohexylperoxy-2,3,3-trimethyl-butane-1,1-dicarbonitrile): ^{1}H NMR ($CDCl_3$): $\delta = 1.02$ (s, 9H), 1.23 (m, 1H, 4′-H), 1.28 (d, $J = 7.1$ Hz, 3H, 2-methyl), 1.30 (m, 2H, 3′-H, 5′-H), 1.42 (m, 2H, 2′-H, 6′-H), 1.54 (m, 1H, 4′-H), 1.77 (m, 2H, 3′-H, 5′-H), 1.94 (m, 2H, 2′-H, 6′-H), 2.16 (q, $J = 3 \times 7.1$ Hz, 1H, 2-H), 4.30 (tt, $J = 2 \times 9.0$, 2×3.6 Hz, 1H, 1′-H). ^{13}C NMR ($CDCl_3$): $\delta = 13.3$ ($2CH_3$), 23.47, 23.48 (C-3′, C-5′), 25.4 (C-4′), 28.7 ($3 \times$ *tert*-butyl-CH_3), 30.13, 30.16 (C-2′, C-6′), 34.2 (C-3), 49.6 (C-2), 76.5 (C-1), 84.0 (C-1′), 113.1 (CN), 114.1 (CN).

9: ^{1}H NMR ($CDCl_3$): $\delta = 1.18$ (s, 9H), 1.83 (dd, $J = 6.6$, 1.7 Hz, 3H), 5.43 (dq, $J = 15.2$, 3×1.7 Hz, 1H), 6.19 (dq, $J = 15.2$, 3×6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 17.5$ (CH_3), 25.3 (CH_3), 39.5 (C), 49.4 (C), 114.2 (CN), 119.4 (CH), 134.2 (CH).

10: ^{1}H NMR ($CDCl_3$): $\delta = 1.22$ (s, 9H), 5.55 (dd, $J = 10.0$, 2.0 Hz, 1H), 5.73 (m, 2H). ^{1}H NMR (C_6D_6): $\delta = 0.75$ (s, 9H), 4.83 (bd, $J = 10.0$ Hz, 1H), 5.09 (dd, $J = 16.5$, 10.0 Hz, 1H), 5.39 (bd, $J = 16.5$ Hz, 1H).

12: (2-(1*R**,2*R**,4*R**-2-*tert*-butoxy-4-*tert*-butyl-cyclohexyl)-malononitrile): ^{1}H NMR ($CDCl_3$): $\delta = 0.84$ (s, 9H), 1.00 (tdd, $J = 2 \times 13.0$, 12.0, 3.5 Hz, 1H, 5′-H_{ax}), 1.15 (tt, $J = 2 \times 12.0$, 2×2.8 Hz, 1H, 4′-H_{ax}), 1.20 (s, 9H), 1.20 (ddd, $J = 12.5$, 12.0, 11.3 Hz, 1H, 3′-H_{ax}), 1.60 (m, 2H, 5′-H_{eq}, 6′-H_{ax}), 1.71 (ddddd, $J = 12.5$, 4.7, 2.8, 2.3, 0.7 Hz, 1H, 3′-H_{eq}), 2.21 (dddd, $J = 15.0$, 3.5, 3.0, 2.8 Hz, 6′-H_{eq}), 2.46 (ddddd, $J = 8.3$, 5.0, 4.7, 2.8, 0.7 Hz, 1H, 1′-H_{eq}), 3.70 (ddd, $J = 11.3$, 5.0, 4.7 Hz, 1H, 2′-H_{ax}), 3.96 (d, $J = 8.3$ Hz, 1H, 2-H). ^{13}C NMR ($CDCl_3$): $\delta = 20.6$ (C-5′), 21.4 (C-2), 27.3 (4″-CH_3), 27.6 (C-6′), 27.9 (2‴-CH_3), 31.1 (C-3′), 32.3 (C-4″), 41.6 (C-1′), 46.6 (C-4′), 70.1 (C-2′), 75.0 (C-2‴), 113.4 (CN), 114.2 (CN).

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