2,6-Dicyano-1,5-dimethyl-4,8-diphenylsemibullvalene. – Synthesis, Structure and the Reactions with Triplet Oxygen[1]

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Addition of trimethylsilyl cyanide to the diphenylbicyclo[3.3.0]octanedione **8c** is catalyzed by the potassium cyanide/18-crown-6 complex and produces a mixture of the diastereomeric bis[*O*-(trimethylsilyl)cyanohydrins] *endo*- and *exo*-**10c** (3:2). The hydrogen fluoride–pyridine complex in phosphorus oxychloride as solvent and, subsequently, an excess of pyridine convert the mixture of diastereomers **10c** into the unsaturated γ,γ'-diphenyldinitrile **11**. This is converted into the red semibullvalene **4** in a single step by treatment with hexachloroethane and concentrated aqueous sodium hydroxide in the presence of tetrabutylammonium hydroxide as phase-transfer catalyst. – Above 30°C, **4** isomerizes in solution to a mixture of the cyclooctatetraenes **12** and **13**. While the red crystals of **4** are stable in the atmosphere, in solution at 20–25°C, **4** reacts readily with triplet oxygen in the dark affording the endoperoxide **16** and the yellow 2*H*-pyran derivative **17** (7:1) which result from parallel reactions. Only at temperatures as high as 110°C, **16** slowly rearranges to **17** which reacts further to yield well-defined but still unknown products. The simultaneous formation of **16** and **17** at low temperatures is interpreted in terms of *endo* and *exo* attack, respectively, of triplet oxygen at the benzylic carbon atoms of the semibullvalene **4** or the isomeric bicyclic diradical **21**. – The structures of the new compounds are based on spectroscopic evidence and X-ray diffraction analyses of **4**, *endo*-**10c**, **11**, **16**, and **17**. The semibullvalene **4** exists as a pair of rapidly rearranging degenerate valence tautomers in solution and in the crystal as well. In the solid state, **4** exhibits apparent C_2 symmetry and equal atomic distances C2–C8 and C4–C6 (201.9 pm). Because true degeneracy is highly unlikely in the crystal, the equal distribution of two non-equivalent valence tautomers at room temperature results from a fortuitous cancelling of the $\Delta H°$ and $T\Delta S°$ terms governing the equilibrium. – The red colour of **4** in the crystal and in solution is due to a maximum at 444 nm which disappears on cooling. Thus, **4** not only belongs to the family of thermochromic semibullvalenes and barbaralanes devoid of a long-wavelength chromophor like **1**, **6**, and **14**, but also shows the most intensive maximum at the longest wavelength observed so far.

The semibullvalene-2,4,6,8-tetracarboxylates **1** and **2**, synthesized by Grohmann et al. (**1**)[2] and Gompper et al. (**2**)[3], are derived from substituted 3,7-dihydroxybicyclo[3.3.0]octa-2,6-dienetetracarboxylates, readily available by the Weiss reaction[4]. The semibullvalene octaester **3** is formed on photolysis of tetrameric dimethyl acetylenedicarboxylate[5]. These semibullvalene polyesters **1**–**3** are interesting because they represent, so far, the only semibullvalenes bearing electron-withdrawing groups at all four termini of the allylic parts, and such semibullvalenes are predicted to exhibit extremely low barriers to the degenerate Cope rearrangement[6].

Unfortunately, conformational ambiguities due to the proximity of ester groups may obscure their π-acceptor property exhibited in unencumbered positions as well as the results of studies aimed at the determination of the Cope activation barriers. We now report on the synthesis and structure of the semibullvalene **4** which has a novel substitution pattern consisting of cyano and phenyl groups at the corners of the Cope system. In fact, the semibullvalenedicarbonitrile **4** does show all extraordinary properties, exhibited to a lesser extent by some other semibullvalenes, in a particularly pronounced way: It is deep red, despite the absence of a long-wavelength chromophor, and thermochromic. Furthermore, **4** isomerizes to the cyclooctatetraenes **12** and **13** at temperatures above 30°C and reacts with triplet oxygen to afford the endoperoxide **16** and the unexpected 2*H*-pyran derivative **17**.

Synthesis of Dicyanodiphenylsemibullvalene 4

The synthesis of **4** parallels the straightforward route which recently has led from the unsaturated diketone **5** to the dicyanodiphenylbarbaralane **6**[7].

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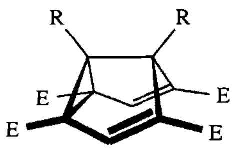

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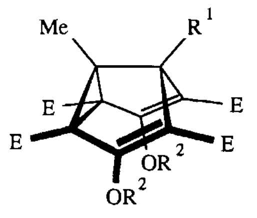
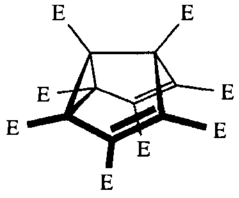


2

E = CO_2Me

	R R
1a	Me Me
1b	$-(CH_2)_3-$
1c	$-(CH_2)_4-$
1d	$-(CH_2)_5-$
1e	$-(CH_2)_6-$

	R^1	R^2
2a	Me	Me
2b	Me	Ac
2c	Et	Me
2d	Et	COPh



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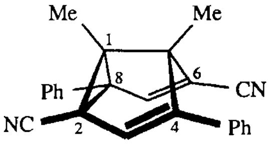

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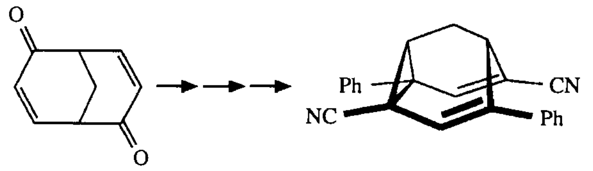
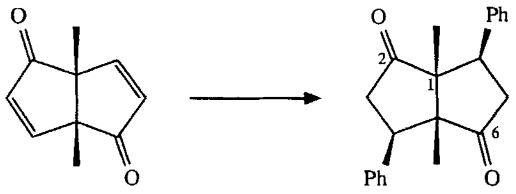


5 **6**

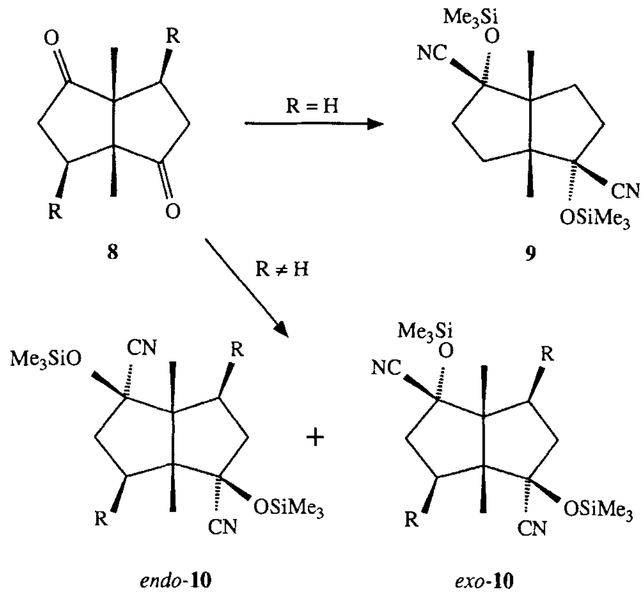


7 **8c**

The cuprate reagent prepared from phenyllithium, cuprous cyanide, and boron trifluoride−diethyl ether adds to the unsaturated ketone **7** exclusively from the *exo* face yielding the diphenyl dione **8c**[8].

The stereoselectivity of the addition of trimethylsilyl cyanide to the 1,5-dimethylbicyclo[3.3.0]octane-2,6-diones **8a** and **b** has been investigated recently[9]. When substituents are lacking at C4 and C8, as in **8a**, catalysis by zinc iodide is efficient (and irreversible[10]) yielding only the *exo,exo* adduct **9**. In the presence of *exo* cyano groups at C4 and C8, on the other hand, the addition of trimethylsilyl cyanide requires catalysis by the potassium cyanide/18-crown-6 complex. Hence, it is reversible[11] and affords predominantly products with the cyano groups attached to the *endo* face, e.g., *endo*- and *exo*-**10b** (7:3)[9]. Likewise, the addition of trimethylsilyl cyanide to **8c** was catalysed by the potassium cyanide/18-crown-6 complex and yielded a mixture of an unsymmetrical *O*-silylated cyanohydrin and one exhibiting C_2 symmetry. While the former could be assigned the structure *exo*-**10c** on the basis of the NMR spectra (Tables 2 and 3), the configuration *endo*-**10c** of the latter was established by an X-ray diffraction analysis (Figure 1, Table 5) of crystals which were obtained from the mixture by recrystallization from methanol.

The conformation of *endo*-**10c** in the crystal closely resembles that of the tetranitrile *endo*-**10b**. Thus, the tips of the cyclopentane envelopes of both *endo*-**10b** and **c** point to the *endo* face of the bicyclo[3.3.0]octane skeleton. This conformation allows the *endo* cyano groups to attain a quasi equatorial position, while the phenyl (in *endo*-**10c**) and the *exo* cyano groups (in *endo*-**10b**) are in a quasi equatorial arrangement. In view of the different steric requirements of phenyl and cyano groups, the similarity of *endo*-**10b** and **c** comes as a little surprise.



8 **9**

endo-**10** *exo*-**10**

	R	*endo*-**10** : *exo*-**10**
8a	H	
8b, 10b	CN	7 : 3[9]
8c, 10c	Ph	6 : 4

The elimination of trimethylsilanol from *O*-silylated cyanohydrins may be performed by the method of Oda et al. involving treatment with phosphorus oxychloride in boiling pyridine[12]. Milder conditions can be applied when, in a first step at lower temperature, the trimethylsilyl group is split off by the action of the hydrogen fluoride−pyridine complex in phosphorus oxychloride as solvent. Subsequently, an excess of pyridine is added, and the elimination is carried out at higher temperature, carefully moni-

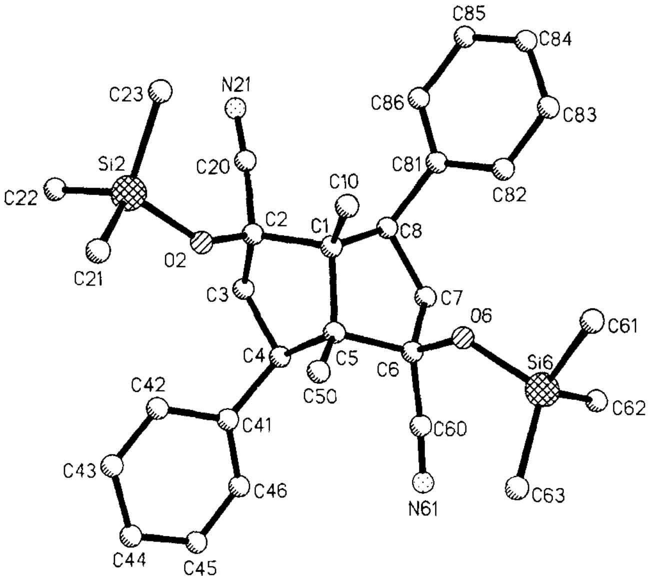
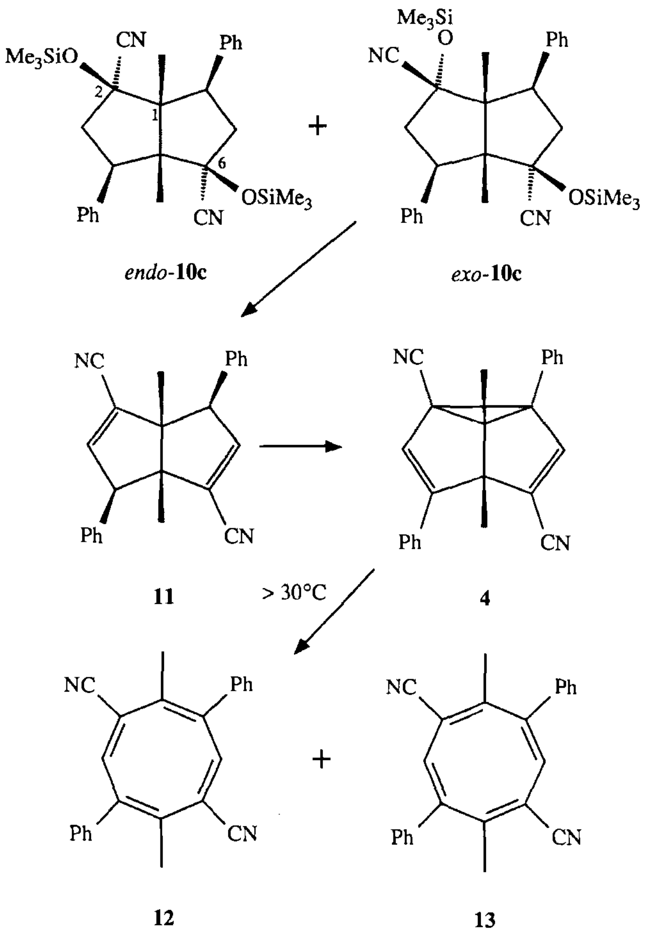


Figure 1. Perspective drawing of the *O*-silylated cyanohydrin *endo*-**10c** showing the numbering of the atoms



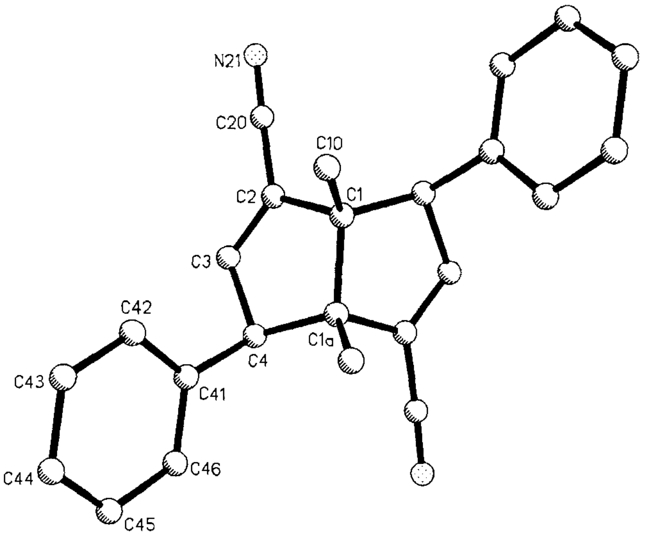


Figure 2. Perspective drawing of the 4,8-diphenylbicyclo[3.3.0]octadienedicarbonitrile **11** showing the numbering of the atoms

tored by HPLC[7,13]. Taking advantage of these modifications, we obtained the α,β-unsaturated dinitrile **11** in high yield from the mixture of *exo*- and *endo*-**10c**. Because phenyl groups interact with CC double bonds more efficiently than cyano groups[14] double bond migration might have taken place under the reaction conditions. Therefore, the structure **11** was confirmed by an X-ray diffraction analysis. Inspection of its result not only reveals the unchanged *exo* configuration of the phenyl groups but also demonstrates the shielding of the bicyclo[3.3.0]octadiene skeleton by the six substituents present.

As a consequence of the highly encumbered allylic systems in **11**, Askani's semibullvalene synthesis, involving bromination by *N*-bromosuccinimide of a bicyclo[3.3.0]octadiene followed by reductive cyclization[15], did not seem promising. Hence, we resorted to a method recently developed for the cyclization of bicyclo[3.3.1]nonadienedicarbonitriles to the corresponding barbaralanedicarbonitriles, e.g. **6**[7] and **15**[16], which can be applied when the allylic hydrogen atoms of the substrate are sufficiently acidic to be removed by concentrated sodium hydroxide under phase-transfer catalysis. The anion thus formed is chlorinated by hexachloroethane. Subsequently, the three-membered ring of the barbaralane is closed in a base-induced dehydrochlorination.

When the unsaturated dinitrile **11** was treated with a mixture of concentrated aqueous sodium hydroxide, dichloromethane, and hexachloroethane in the presence of tetrabutylammonium hydroxide under argon, it was gratifying to observe a fast reaction indicated by HPLC and the development of a deep brown colour. Careful work-up of the reaction mixture at low temperature followed by chromatography and crystallization from ethyl acetate afforded a 51% yield of red crystals, melting with decomposition at 134–136°C, which persisted unchanged in the laboratory atmosphere at ambient temperature. Solutions of the red crystals exhibit a red colour which slowly changes to pale yellow in the presence of atmospheric oxygen (see below). Even degassed solutions fade at temperatures above room temperature because a mixture of the colourless cyclooctatetraenes **12** and **13** is formed. A detailed study of this thermal rearrangement will be reported separately[17].

The expected molecular formula of the red crystals was confirmed by the high-resolution mass spectrum. The electron impact-induced mass spectrum at low resolution is characterized by a strong peak of the molecular ion which primarily loses a hydrogen atom, a methyl group, or hydrogen cyanide. The close similarity of the mass spectra of **4** and of the isomeric cyclooctatetraenes **12** and **13**[17] lends credibility to the assumption that their molecular ion is formed from **4** in the mass spectrometer.

Table 1. Yields, melting points, and IR spectroscopic data of some bicyclo[3.3.0]octadienes, dicyanodiphenylsemibullvalene **4**, the endoperoxide **16**, and the 2*H*-pyran **17**

Cpd.	Yield [%]	M.p. [°C]	IR [cm^{-1}] (KBr) C=C	C≡N
4	51	134 – 136 (dec.) (ethyl acetate)	1595	2217 2208[a,b]
exo-, *endo-***10c** (2 : 3)	79	217 – 220		
*endo-***10c**		223 – 225 (methanol)		2240
11	78	245 – 247 (acetone)	1623 1596	2212[b]
16	26[c]	149 – 150 (dec.) (tetrahydrofuran)		2214[b]
17	11[c]	155 – 157 (dec.) (CH_2Cl_2)	1657 (C=O) 1619	2221[b]

[a] IR spectra (trichloromethane): $\tilde{\nu}$ = 2221, 2213; (paraffin oil): 2215, 2206; (RbI): 2217, 2209 cm^{-1}. – [b] IR spectra (tetrahydrofuran), **4**: 2219 sh, 2213 cm^{-1}; **11**: 2216; **16**: 2220; **17**: 2222 cm^{-1}. – [c] Yield based on **11**.

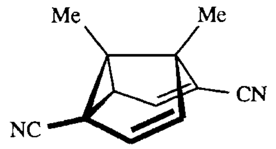
NMR, IR, and UV/Vis Spectra of Dicyanodiphenylsemibullvalene 4

The proton (Table 2) and carbon-13 spectra (Table 3) of solutions of semibullvalene **4** are compatible with two degenerate valence tautomers rearranging rapidly relative to the NMR time scales. On the basis of the low-temperature carbon-13 spectra of dicyanosemibullvalene **14**[18] one can expect that, with the present instruments, exchange broadening in the spectra of **4** may be observed only at extremely low temperatures (<110 K) if at all. Therefore, such measurements have not been attempted.

The infrared spectra of semibullvalene-2,6-dicarbonitrile **14**[18] and barbaralane-2,6-dicarbonitrile (**15**)[19] are characterized by two nitrile bands which have been assigned to cyano groups at a cyclopropane ring and to α,β-unsaturated cyano groups, respectively. This assignment is supported by the size of the C≡N frequency of cyclopropanecarbonitrile (2235 cm^{-1}, in tetrahydrofuran solution) and the α,β-unsaturated nitriles that are precursors of **14**[18] and **15**[19]. As shown by a comparison of the barbaralanes **6** [$\tilde{\nu}$(C≡N) = 2229 and 2209 in dichloromethane solution[7], 2231 and 2209 cm^{-1} in tetrahydrofuran solution] and **15** [$\tilde{\nu}$(C≡N) = 2240 and 2217 cm^{-1} in tetrachloroethene solution[19]], phenyl groups at C4 and C8 of the barbaralane-2,6-dicarbonitrile system lower the wavenumbers of both nitrile absorptions by about 10 cm^{-1}. Considering the IR spectrum of **14** [$\tilde{\nu}$(C≡N) = 2231 and 2218 cm^{-1} in tetrachloroethene solution[18]], one may hence expect nitrile bands around 2220 and 2208 cm^{-1} in the IR spectrum of **4**.

The infrared spectra have been taken from potassium bromide discs and tetrahydrofuran solutions because the compounds are most soluble in this solvent which is also sufficiently transparent in the range of C≡N bands. Furthermore, IR spectra have been run from **4** in trichloromethane solutions, Nujol mulls, Fluorolube[20] mulls, and rubidium iodide[21] discs.

In fact, the IR spectra of **4** did exhibit two nitrile absorptions in the expected range (Table 1) which, surprisingly, were accompanied by a sharp band at considerably lower frequencies [$\tilde{\nu}$ = 2191 cm^{-1} (m, $CHCl_3$); 2183 (w, Nujol); 2182 (w, Fluorolube); 2182 (m – s, KBr); 2183 (s, RbI)]. In the IR spectrum of a tetrahydrofuran solution, two bands of medium intensity were observed instead (2199, 2187 cm^{-1}). The intensities of the extraordinary band ranged from weak to strong, according to the particular sample. When the organic material from a potassium bromide disc was dissolved in dichloromethane and analysed by HPLC, only minor impurities could be detected (<5%) which had not been present before. For these reasons, we assign the low-frequency band to small amounts of an unknown, labile species that exhibits an unusually strong IR absorption[22].



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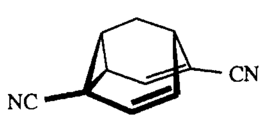


15

Dimethyl 1,5-dimethylsemibullvalene-2,6-dicarboxylate[23]. The semibullvalenetetracarboxylates **1**[2], and dicyanosemibullvalene **14**[18] are yellow, 2,4,6,8-tetraphenylbarbaralane[24] and dicyanodiphenylbarbaralane **6**[7] are orange-red compounds devoid of a long-wavelength chromophor. All exhibit thermochromism in solution and the solid state. Both properties have recently been interpreted in terms of a model based on the approximate shape of the energy surface of the ground and excited states, e.g., a shallow double minimum and a narrow, steep trough, respectively[24]. While the UV/Vis spectra of the semibullvalenes and barbaralanes mentioned above exhibit only long-wavelength shoulders except barbaralane **6**, which has a true maximum at 436 nm (lg ε = 2.79 in acetonitrile at 295 K)[7], the spectrum of **4** is characterized by a nicely separated maximum at 444 nm (lg ε = 3.235 in acetonitrile, Figure 3). As expected, **4** is thermochromic, i.e. crystals and solutions reversibly turn orange on cooling. These observations contribute strongly to the evidence supporting the hypothesis that colour in the absence of long-wavelength chromophors, thermochromism, and extremely low barriers to the degenerate Cope rearrangement are interrelated properties of semibullvalenes and barbaralanes that are characterized by very flat double-minimum ground states.

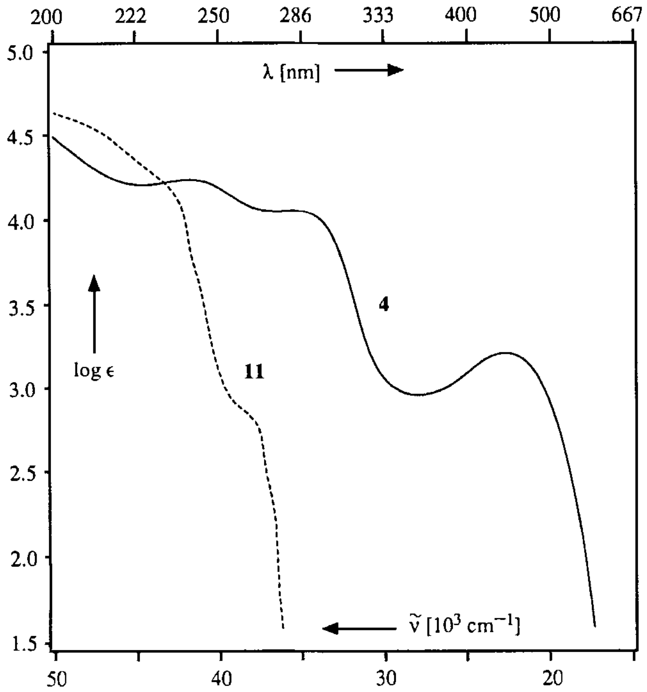


Figure 3. UV/Vis spectra of dicyanodiphenylsemibullvalene **4** and, for comparison, of its precursor **11**, both taken from solutions in acetonitrile at 295 K

Structure of Dicyanodiphenylsemibullvalene 4

The structure in the crystal of a considerable number of semibullvalenes has been determined by X-ray diffraction analyses[25]. The apparent atomic distances C2–C8 and C4–C6 in the crystalline state of semibullvalenes that undergo a *degenerate* Cope rearrangement *in solution* vary over a wide range. They are even seemingly equal in 2,6-dibromo-1,5-dimethylsemibullvalene-3,7-dicarbonitrile [186.5(10) pm] and the β-form of semibullvalene-2,6-dicarbonitrile **14** [199.0(4) and 199.6(4) pm]. By means of variable-temperature solid-state carbon-13 spectroscopy, it has been demonstrated that the observation of anomalous C2–C8 and C4–C6 distances in X-ray structures is a consequence of dynamic disorder associated with a rapid *nondegenerate* Cope rearrangement[26]. The result of an X-ray diffraction analysis of **4** is shown in Figure 4.

As shown by Figure 4, **4** exhibits apparent C_2 symmetry in the crystal and hence equal C2–C8 and C4–C6 distances (201.9 pm). The shape of the thermal displacement ellipsoids at C2, C4, C6, and C8 is, however, indicative of a dynamic disorder resulting from a Cope rearrangement. This excludes a static C_2 symmetrical, delocalized molecular structure. The apparent C_2 symmetry in the crystal is due to the fact that, *at the temperature of the experiment*, two rapidly rearranging valence tautomers are present in equal proportions, i.e. the equilibrium constant K at room temperature is 1 or very close to 1. While $K = 1$ *at every temperature* holds for *truly degenerate* valence tautomers because, by definition, $\Delta H° = 0$ and $\Delta S° = 0$, the observation of $K \approx 1$ and hence $\Delta G° \approx 0$ means that the enthalpy ($\Delta H°$) and the enthalpy terms ($T\Delta S°$) governing the equilibrium of non-equivalent valence tautomers fortuitously cancel each other. A decision between these models may be reached after variable-temperature X-ray diffraction analyses or solid-state carbon-13 spectra have been performed. Though such experiments have not been carried out so far, the latter model is more plausible and has already precedence in the β-modification of dicyanosemibullvalene **14**[26].

The sum of the atomic distances (C2–C8 + C4–C6) in semibullvalenes, determined by X-ray crystallography, may be regarded as a molecular property. This sum varies between 385 and 399 pm in the 15 semibullvalenes investigated so far, and the values for very fast rearranging semibullvalenes are found at 397–399 pm[25]. The value for **4** (404 pm) is significantly larger and just another of the extreme properties of this system.

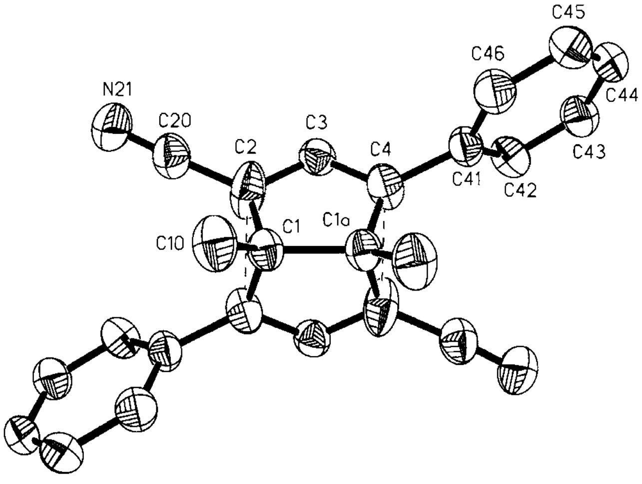


Figure 4. Perspective drawing (ORTEP plot) of dicyanodiphenylsemibullvalene **4** showing the numbering of the atoms and the thermal displacement ellipsoids

Reactions of Dicyanodiphenylsemibullvalene 4 with Triplet Oxygen

Several semibullvalenes, e.g., octamethylsemibullvalene[27], the 1,5-bridged semibullvalenetetracarboxylates **1b** and **c**[2b], and octamethyl semibullvaleneoctacarboxylate (**3**)[5] are reported to react with triplet oxygen. Apart from **3**, whose product with oxygen is still unknown, the other semibullvalenes yield endoperoxides in which the peroxide bridge connects C2 and C6 (**1b** and **1c**) or C2 and C8 (octamethylsemibullvalene and **1b**). Grohmann et al. interpreted the endoperoxide formation in terms of 2,6- and 2,8-trapping of triplet bicyclo[3.3.0]octadienyl diradicals with oxygen though a direct attack at the semibullvalenes could not be ruled out[2b].

When a red solution of **4** in dichloromethane is stirred in an open vessel in the dark for three days, the colour turns pale yellow, semibullvalene **4** disappears, and two products are formed as monitored by HPLC. The major product is only little soluble and crystallizes as colourless needles. Likewise, a dilute solution of **4** in trichloromethane turns almost colourless within one day, while the $C{\equiv}N$ bands of **4** in the IR spectrum, including the extraordinary band at 2191 cm^{-1} (see above), are replaced by a single absorption at 2225 cm^{-1}, and small needles appear. Separation of the mixture by medium-pressure liquid chromatography afforded colourless crystals, m.p. 149–150°C (dec.), as the first fraction and yellow crystals, m.p. 155–157°C (dec.), as the second one in a ratio of 7:3.

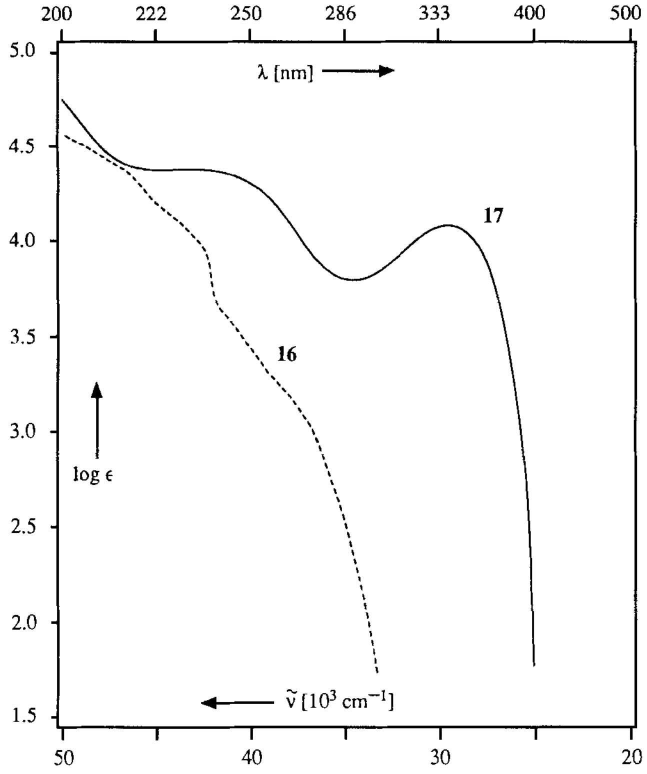


Figure 5. UV/Vis spectra of the endoperoxide **16** and the isomeric 2*H*-pyran derivative **17**, both taken from solutions in acetonitrile at 295 K

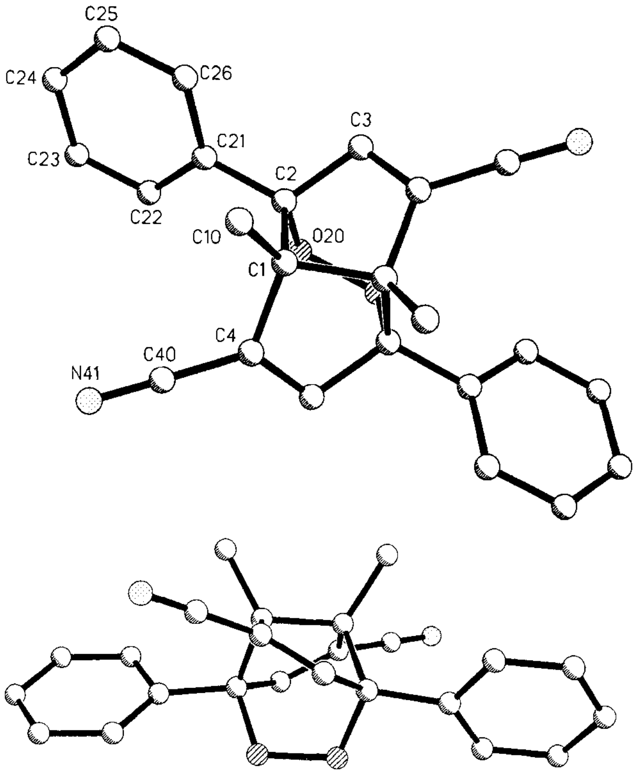


Figure 6. Perspective drawing of the endoperoxide **16**, obtained from semibullvalene **4** and triplet oxygen, showing the numbering of the atoms (above), and a different view (below)

The molecular formulae, based on elemental analyses and mass spectra, of both products correspond to the addition of one mole of oxygen to semibullvalene **4**.

Their UV/Vis spectra differ significantly (Figure 5), attesting to the presence of a long-wavelength chromophor in the yellow compound which is not compatible with an endoperoxide structure. The proton (Table 2) and carbon-13 spectra (Table 3) of the colourless product show that it has C_2 symmetry and two equivalent partial structures of an α,β-unsaturated nitrile. Taken together with the features of the IR, UV, and mass spectra, the spectroscopic evidence strongly supports the endoperoxide structure **16** in which the oxygen atoms have been attached to the benzylic carbon atoms of **4**. Eventually, this structure was established by an X-ray diffraction analysis (Figure 6).

The yellow oxygen product does not possess any symmetry. Though the existing spectroscopic evidence, including ^{13}C,^{1}H-COSY spectra, attested to the presence of certain partial structures, e.g., a benzoyl group, α,β-unsaturated nitrile functionalities, a methyl group attached to a saturated and one to an olefinic carbon atom etc., a definitive structure was not derived. Further spectroscopic scrutinity was obviated by an X-ray diffraction analysis which established the unexpected 2*H*-pyran structure **17** for the yellow product formed by the reaction of **4** with triplet oxygen (Figure 7).

The yellow 2*H*-pyran derivative **17** may be derived by an electrocyclic ring closure from the symmetrical 1,8-diphenyloctatriene-1,8-dione **18** which in turn may be regarded as the product of a thermal [2 + 2 + 2] cycloreversion of the endoperoxide **16**. Cleavage of the peroxide bond, removal of strain, and formation of the highly conjugated system **18** might provide the driving force for a *simultaneous* cleavage of three σ bonds for which only little precedence can be found, however[28a]. Indeed, the formally related 3σ → 3π thermal isomerization of 3-heteroquadricyclanes occurs by a *two-step* mechanism[28b]. Alternatively, the process **16** → **18** may occur stepwise initiated by breaking of the oxygen–oxygen bond (see below). However that may be, when a degassed solution of **16** in [D$_6$]benzene, containing 1,3,5-tri-*tert*-butylbenzene as internal standard, was heated to 110°C, traces of **17** began to appear after one hour, as shown by the proton spectra. While decomposition of **16** was still very slow at this temperature (3% per h), after one hour at 130°C, as much as 63% of **16** had disappeared. Only 14% of **17** could be detected, however, because a large fraction of **17**, formed primarily, had reacted further to yield

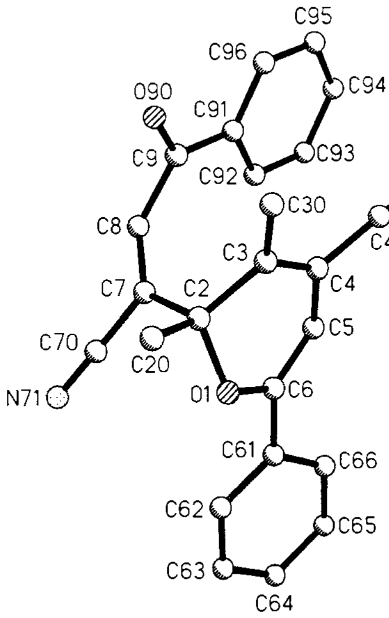
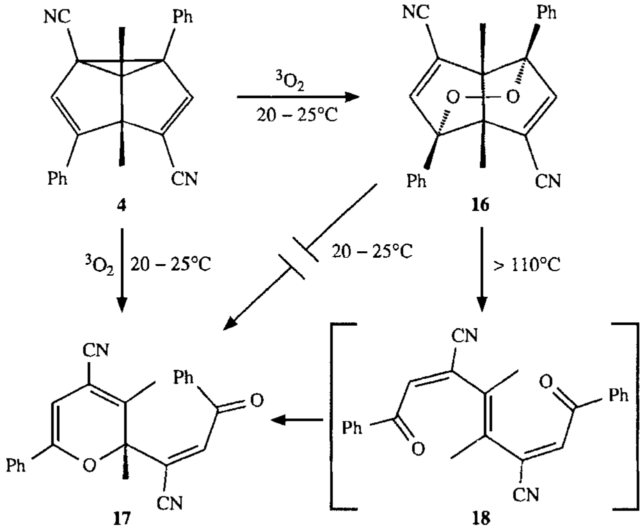
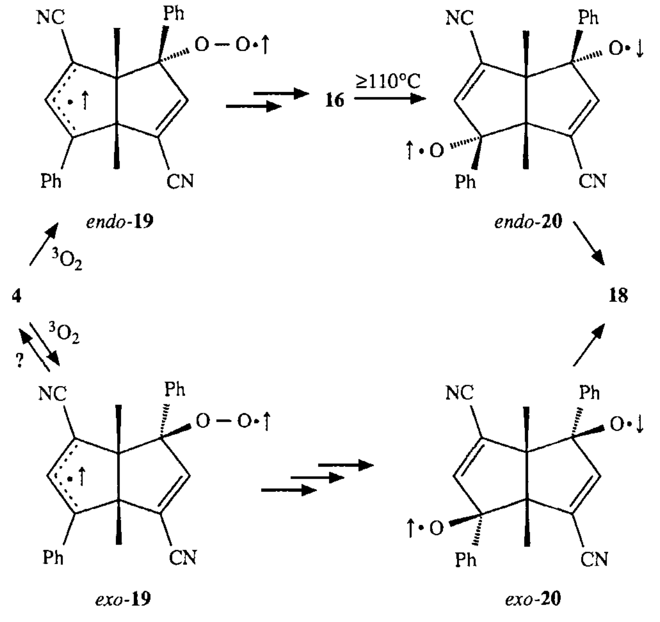
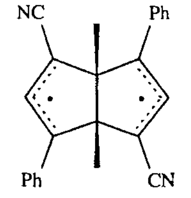


Figure 7. Perspective drawing of the 2*H*-pyran **17**, obtained from dicyanodiphenylsemibullvalene **4** and triplet oxygen, showing the numbering of the atoms

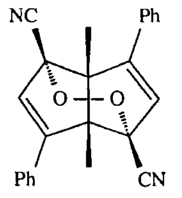
well-defined but still unknown products. The same products arose when a degassed solution of **17** in [D$_6$]benzene was heated to 90°C in a separate experiment. After one hour, 85% of **17** had reacted to the unknown products which did not change any more within one hour at 145°C. Therefore, we conclude that **17** may be formed on thermolysis of the endoperoxide **16**, and both exhibit similar, moderate thermal stability.







21



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There must be a second mechanism, however, which accounts for the formation of the yellow 2*H*-pyran **17** *at low temperature* under the conditions which prevailed when the semibullvalene **4** reacts with oxygen, because **16** is perfectly stable under these conditions. Monitoring the oxygenation by proton spectroscopy immediately revealed that **16** and **17** are formed in *parallel* reactions. Both appeared already after five minutes at conversions of **4** as low as 9% in a [D$_2$]dichloromethane solution saturated with oxygen and containing 1,3,5-tri-*tert*-butylbenzene as internal standard (→ **4**:**16**:**17** = 91:6:3). The ratio of **4**, **16**, and **17** did not alter significantly within the next hour. Thereafter, oxygen was briefly introduced again changing the ratio slowly to 43:49:8. The third introduction of oxygen after three hours eventually resulted in a ratio of 11:78:11. No other products could be detected during and after the oxygenation reaction.

We assume that **16** and **17** result from *different directions* of attack at semibullvalene **4** or its ring-opened isomer, i.e. the singlet diradical **21**. Formation of **16** is initiated by the attack of triplet oxygen at the *endo* face leading to the *endo*-peroxy triplet diradical *endo*-**19** which may eventually cyclize after spin inversion. According to Barton and coworkers[29], three mechanisms avoid the spin barrier in reactions of organic substrates with triplet oxygen: Two are catalysed by electrophilic species, the third is restricted to compounds that are destabilised by strain or reasonance with respect to the peroxide[30] and does not require catalysis. The latter mechanism involves spin inversion by exchange via the formation and decomposition of tetraoxides[29] and may be invoked to explain the spin inversion of *endo*-**19**.

The low-temperature mode of formation of **17**, which does *not* involve the endoperoxide **16**, is more difficult to interpret. Attack of triplet oxygen at the *exo* face affords the *exo*-peroxy triplet diradical *exo*-**19** which does not undergo an *intra*molecular reaction. It rather initiates a copolymerization[31] of oxygen and semibullvalene **4** which eventually affords oligomeric or polymeric peroxides. Alternatively, oligomeric or polymeric tetraoxides may be formed[32]. At any case, the hypothetic intermediates are labile and decompose to the bis(*exo*-oxyl) diradical *exo*-**20** which fragments into octatriendione **18**. Support for the hypothetical bis(*exo*-oxyl) diradical *exo*-**20** may be provided by the thermal cleavage of the endoperoxide **16** to the octatrienedione **18**. Though being allowed on a synchronous reaction path, this decomposition probably starts with breaking the oxygen–oxygen[33] bond to afford the diastereomeric bis(*endo*-oxyl) diradical *endo*-**20** which fragments into **18**.

The product from the *endo* attack of oxygen, i.e., the endoperoxide **16**, predominates over the 2*H*-pyran **17**, which is postulated to result from an *exo* attack. According to the species which is attacked, semibullvalene **4** or the isomeric diradical **21**, the large **16**:**17** ratio is to be interpreted in two different ways. In electrophilic addition reactions, e.g., of bromine[34] and 4-phenyl-1,2,4-triazoline-3,5-dione[35], semibullvalenes exclusively suffer *exo* attack with concomitant cleavage of the cyclopropane C2–C8 bond. For the same stereoelectronic cause, formation of this bond in a bicyclo[3.3.0]octadiene by an elimination reaction is only possible if the leaving groups attain the *exo* configuration[36]. The same face selectivity most probably governs the addition of triplet oxygen. As basis for an explanation of the seemingly contradicting large **16**:**17** ratio, reversibility may be invoked of the *exo* attack. Thus, only a minor fraction of *exo*-**19** is converted into **17** while the major fraction reverts to oxygen and **4** which reacts slowly but virtually irreversibly with oxygen to afford *endo*-**19** and eventually the endoperoxide **16**. On the other hand, if the diradical **21** is the reacting species, a different face selectivity prevails, i.e., that of bicyclo[3.3.0]octadienes. As shown by the addition of trimethylsilyl cyanide to the bicyclo[3.3.0]octane-2,6-diones **8**, the face selectivity of the addition at trigonal planar centres of the bicyclo[3.3.0]octane system is strongly influenced by the substitution pattern. The same conclusion can be derived from the results of allylic bromination reactions of bicyclo[3.3.0]octadienes[36]: The inherent preference for *exo* attack is changed by encumbering substituents resulting eventually in a predominance of the *endo* products, e.g., *endo*-**10b** and -**c**. Therefore, an *endo* face selectivity is not unlikely for the diradical **21** which bears no less than six substituents.

The question remains as to why no products are observed which result from an attack of oxygen at a carbon atom that bears a cyano group, e.g., **22**. Provided that such compounds did not escape detection, their absence may be taken as a hint that not the semibullvalene **4** but the bicyclic diradical **21** is attacked whose reactivity toward oxygen is higher at the benzylic carbon atoms than at the carbon atoms next to the nitrile groups. This regioselectivity is in accord with the well-established fact that phenyl groups stabilize radical centres better than nitrile groups[37] and may hence be explained in terms of an uneven spin distribution at the termini of the allylic systems in the diradical **21**.

Concluding Remarks

The series of semibullvalenetetracarboxylates **1** and **2** are characterized by four electron-withdrawing substituents at positions where theory predicted a particularly low Cope barrier as a consequence[6]. In the dicyanodiphenylsemibullvalene **4**, on the other hand, these positions are occupied by substituents that differ considerably in their electronic effects. Thus, **4** may be regarded as a donor/acceptor-substituted semibullvalene of a type hitherto not considered by theory[6]. The results described in this paper suggest that such a substitution pattern may even enhance the unusual properties exhibited by semibullvalenes carrying *only* acceptor groups.

While the semibullvalenetetracarboxylates **1** and **2** clearly reflect the substitution pattern of their bicyclic precursors, i.e., the tetraesters obtained by the Weiss reaction[4], the synthesis of semibullvalene **4** is the first execution of a more variable *building-block* strategy which allows us to introduce electron acceptor and/or donor groups that finally appear at the four allylic corners of the semibullvalene skeleton. Highly substituted semibullvalenes of this sort are attractive synthetic targets because they promise exceptional physical properties as well as unusual reactions. Work towards a realization of further examples is in progress.

We thank Professor *W. R. Roth*, Bochum, for stimulating discussions concerning the oxygen reaction of semibullvalenes. We are indebted to Professor *W. Schenk*, Institut für Anorganische Chemie, Universität Würzburg, for the access to the infrared spectrometer Perkin-Elmer 283. We thank Mrs. *E. Ruckdeschel* and Dr. *D. Scheutzow* for recording NMR spectra and Dr. *G. Lange* and Mr. *F. Dadrich* for measuring mass spectra. Financial support by the *Fonds der Chemischen Industrie*, Frankfurt am Main, is gratefully acknowledged.

Experimental

Yields, melting points, and IR: Table 1. – ^{1}H NMR: Table 2. – ^{13}C NMR: Table 3. – Molecular formulae and masses, and elemental analyses: Table 4. – Melting points: Sealed capillary tubes, apparatus from Büchi, Flawil, Switzerland. – IR: Perkin-Elmer 1420; $C\equiv N$ bands: Perkin-Elmer 283, calibrated with trichloromethane. IR spectra of tetrahydrofuran and trichloromethane solutions were taken in 1-mm NaCl cells. – ^{1}H NMR: Bruker AC 200 (**4**, 0.153 Hz/pt.), AC 250 (0.305 Hz/pt.) and WM 400 (**17**, 0.056 Hz/pt.). In order to resolve close signals and small long-range couplings, we carried out a Lorentzian-to-Gaussian line-shape transformation[38]. – ^{13}C NMR: Bruker AC 200, AC 250 and WM 400. The signals were assigned on the basis of DEPT or ^{13}C,^{1}H COSY spectra (**17**). – 70-eV MS: Finnigan MAT 8200. The exact mass of **4** was determined by peak matching after calibration with perfluorokerosene. – UV: Hitachi U 3200, $[\varepsilon] = [1\ \mathrm{mol^{-1}\ cm^{-1}}]$. The solution of **4** in acetonitrile was prepared in a closed apparatus, equipped with 0.1- and 1.0-cm quartz cells, repeatedly degassed in vacuo and with ultrasonic irradiation, and saturated with argon.

High-performance liquid chromatography (HPLC): Waters M-6000A equipped with UV detector 440 (λ = 254 nm) and RI detector R401, (250 × 4.6) mm stainless steel column packed with LiChrosorb Si60, 5 μm (Merck), 0.6 ml/min petroleum ether (b.p. 50–70°C) (PE)/ethyl acetate (EA) (90:10), retention time t_R [min] = 10.8 (*exo*-**10c**, *endo*-**10c**), 15.3 (**11**); 1.0 ml/min, t_R = 5.8 (**11**); 1.5 ml/min, t_R = 3.7 (**11**), 4.4 (**12**), 4.8 (**13**), 7.1 (**4**), 8.7 (**16**),

Table 2. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton spectra of some bicyclo[3.3.0]octadienes, the semibullvalene **4**, and its products with triplet oxygen **16** and **17** recorded from [D]trichloromethane solutions. Chemical shifts of protons that are equivalent in virtue of symmetry (*endo*-**10c**, **11**, **16**) or a rapid degenerate Cope rearrangement (**4**) are given only once

Cpd.	H_A	H_B	H_X	$^2J_{AB}$	$^3J_{AX}$	$^3J_{BX}$	Me	Ph	Me_3Si
exo-**10c**[a]	2.54	2.629	4.25	13.2	13.4	5.1	0.56	7.2 – 7.6	0.25
	2.50	2.635	4.39	12.9	5.9	12.1	0.81	–	0.43
endo-**10c**	2.53	3.12	3.69	14.6	11.2	4.7	0.78	7.3 – 7.6	0.32
11	6.62	–	4.21	–	2.9	–	0.69	7.1 – 7.4	–
		=CH–							
4		6.11					1.47	7.4 – 7.5	
16		7.15					0.92	7.3 – 7.5	
17[b]		5.67, 7.34					1.80, 2.12	7.2 – 7.7	

[a] The data were recorded from a mixture of *exo*- and *endo*-**10c** (2:3). – [b] 400 MHz, 0.056 Hz/pt.

10.1 (**17**). – Preparative medium-pressure liquid chromatography[39] (MPLC): Pump FC1 equipped with pump head K110 and 0.2-l pulse damper (LEWA, Leonberg), UV detector Knauer 87.00 (λ = 254 nm), and RI detector Bischoff 8110, (70 × 7) cm glass column packed with LiChroprep Si60, 15–25 μm (Merck), 70 ml/min PE (b.p. 30–50°C/EA (90:10), 15 bar.

Dichloromethane and ethyl acetate were distilled from diphosphorus pentoxide, pyridine from calcium hydride under N_2, diethyl ether and tetrahydrofuran from sodium/potassium alloy under Ar. – Phosphorus oxychloride was distilled under N_2 immediately before use. Potassium cyanide was dried at 120°C/5 · 10^{-2} Torr over potassium hydroxide. – Potassium cyanide/18-crown-6 complex[11], phenyllithium[40], and **7**[41] were prepared according to literature procedures.

1,5-Dimethyl-4,8-diphenylbicyclo[3.3.0]octane-2,6-dione (**8c**): To a stirred suspension of copper(I) cyanide (1.35 g, 15 mmol) in tetrahydrofuran (120 ml) under N_2, a freshly prepared solution of phenyllithium in diethyl ether (2.2 M, 13.5 ml; 2.50 g, 30 mmol) was added slowly at –78°C followed by boron trifluoride–diethyl ether (3 ml, 24 mmol). After stirring for 5 min, a solution of **7** (810 mg, 5.0 mmol) in tetrahydrofuran (30 ml) was added dropwise within 30 min. Stirring at –78°C was continued until complete conversion (HPLC, 2 h). After the temperature of the reaction mixture had attained 20–25°C, aqueous 2 M ammonium hydroxide (10 ml) and a saturated aqueous solution of ammonium chloride (80 ml) were added, and the mixture was extracted with diethyl ether (4 × 150 ml). The combined organic layers were extracted with a saturated aqueous solution of ammonium chloride (4 × 30 ml) and dried with sodium sulphate. After distillation of the solvent in vacuo, the pale brown residue was dissolved in dichloromethane (30 ml), and the solution was filtered through silica gel (30 g, 32–63 μm) which was eluted with dichloromethane (100 ml). After distillation of the solvent in vacuo, the pale yellow solid was triturated with hot hexane (20 ml). Drying in vacuo yielded a colourless solid (1.10–1.18 g, 69–72%, 12 runs), m.p. 183–185°C, which was pure enough for further use (ref.[8] 87%, m.p. 184–186°C).

Table 3. Chemical shifts (δ values) in carbon-13 spectra of some bicyclo[3.3.0]octadienes, the semibullvalene **4**, and the endoperoxide **16** recorded from [D]trichloromethane solutions. Chemical shifts of carbon-13 atoms that are equivalent in virtue of symmetry (*endo*-**10c**, **11**, **16**) or a rapid degenerate Cope rearrangement (**4**) are given only once

Cpd.	C-1 C-5	C-2 C-6	C-3 C-7	C-4 C-8	Me	Me_3Si
4	67.8	90.1	128.9	116.0	13.7	
exo-**10c**[a]	60.5	76.9	43.9	41.3	16.6	1.18
	61.9	81.1	44.2	49.2	20.5	1.40
endo-**10c**	64.6	81.4	46.5	50.1	17.1	0.94
11	61.6	125.5	145.2	59.4	19.6	
16	68.2	122.6	144.8	95.7	12.8	

Cpd.	CN	*ipso*-C	*o*-C, *m*-C	*p*-C
4	118.5	132.9	129.22, 129.46	129.01
exo-**10c**[a]	120.4	138.40	128.02, 128.35	126.91
	121.9	138.47	128.27, 128.44	126.94
endo-**10c**	120.9	141.0	127.8, 130.0	126.7
11	115.5	137.1	128.96	128.04
16	114.5	133.3	126.1, 129.3	130.4

[a] The data were recorded from a mixture of *exo*- and *endo*-**10c** (2:3).

Table 4. Molecular formulae, masses, and elemental analyses for some bicyclo[3.3.0]octadienes, the semibullvalene **4**, and its oxygen products **16** and **17**

Cpd.		Molecular Mass	Elemental Analysis	C	H	N
4	$C_{24}H_{18}N_2$	334.4[a]	Calcd.	86.20	5.42	8.38
			Found	86.34	5.72	8.53
exo-, *endo*-**10c** (2 : 3)	$C_{30}H_{40}N_2O_2Si_2$	516.8	Calcd.	69.71	7.80	5.42
			Found	70.01	7.82	5.45
11	$C_{24}H_{20}N_2$	336.4	Calcd.	85.68	5.99	8.33
			Found	85.50	6.03	8.46
16	$C_{24}H_{18}N_2O_2$	366.4	Calcd.	78.67	4.95	7.65
			Found	78.36	5.05	7.24
17	$C_{24}H_{18}N_2O_2$		Found	78.60	4.85	7.64

[a] Exact mass calc. 334.1470; found 334.1460.

*1,5-Dimethyl-4,8-diphenyl-2,6-bis(trimethylsiloxy)bicyclo[3.3.0]octane-2,6-dicarbonitrile, Mixture of Diastereomers exo- and endo-***10c**: To a stirred mixture of **8c** (7.71 g, 24 mmol) and the potassium cyanide/18-crown-6 complex (1.70 g, 5.2 mmol)[11] under N_2, trimethylsilyl cyanide (7.0 ml, 55 mmol) was added at 0°C. Stirring was continued at 20–25°C and the clear, yellow solution slowly solidified. Dichloromethane (11 ml) was added after 10 min. After 3.5 h, a saturated aqueous solution of potassium dihydrogenphosphate (35 ml) was added which caused the evolution of hydrogen cyanide

Table 5. Experimental details and results of the X-ray diffraction analyses of **4**, *endo*-**10c**, **11**, **16** and **17**

Compound		**4**	*endo*-**10c**	**11**	**16**	**17**
Molecular formula		$C_{24}H_{18}N_2$	$C_{30}H_{40}N_2O_2Si_2$	$C_{24}H_{20}N_2$	$C_{24}H_{18}N_2O_2$	$C_{24}H_{18}N_2O_2$
Molecular mass		334.42	516.83	336.44	366.42	366.42
Crystal system		monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group		C2/c	P2$_1$/n	C2/c	C2/c	P2$_1$/n
a [pm]		2122.6(7)	2065.0(5)	2210.8(6)	1244.2(2)	1686.9(9)
b [pm]		627.5(2)	1139.9(3)	596.0(1)	972.2(2)	1062.6(3)
c [pm]		1406.2(3)	1301.3(3)	1571.8(5)	1590.1(3)	1121.1(3)
β [°]		110.56(2)	94.56(2)	114.98(2)	104.54(1)	106.60(4)
V [pm^3] $\cdot$ 10^{-6}		1753.8(9)	3054(1)	1877(1)	1862.3(6)	1926(1)
Z		4	4	4	4	4
d (calcd.) [g cm^{-3}]		1.266	1.124	1.190	1.307	1.263
Size of crystal [mm]		0.4x0.55x0.15	0.35x0.75x0.15	0.25x0.25x0.85	0.3x0.6x0.2	0.6x0.7x0.25
Range	(h)	0 – 27	0 – 26	0 – 28	0 – 16	0 – 21
	(k)	0 – 8	0 – 14	0 – 7	0 – 12	0 – 13
	(l)	–18 – 17	–16 – 16	–20 – 18	–20 – 20	–14 – 13
No. of measured reflections		2247	7685	2421	2357	4884
Symmetry-independent reflections		2017	7039	2167	2145	4426
Observed reflections $F>3\sigma(F)$		1420	4391	1801	1876	3554
Linear absorpt. coeff. [mm^{-1}]		0.07	0.14	0.07	0.08	0.08
Absorption correction		ψ-Scan	ψ-Scan	ψ-Scan	ψ-Scan	ψ-Scan
Ratio F_{obs}/parameters		11.93	13.51	14.76	14.66	13.99
R		0.069	0.080	0.048	0.046	0.055
R_w		0.053	0.059	0.045	0.048	0.053
Diff. Four.	$\Delta\rho_{max}$[*] [eÅ^{-3}]	0.31	0.24	0.17	0.29	0.32
	$\Delta\rho_{min}$[**]	0.27	0.23	0.14	0.17	0.30

[*] Maximum and [**] minimum of the remaining electron density in the final differential Fourier synthesis.

(**Attention!**). The mixture was extracted with dichloromethane (3 × 150 ml). The combined organic layers were extracted with a mixture of a saturated aqueous solution of potassium dihydrogenphosphate and water (1:1, 3 × 50 ml) and dried with sodium sulphate. After distillation of the solvent in vacuo, the red, waxy solid was dissolved in dichloromethane (60 ml), and the solution was filtered through silica gel (50 g, 32–63 μm) which was eluted with dichloromethane (160 ml). The resulting pale yellow solution was concentrated to 20 ml in vacuo, cooled to 0°C for 1 d, and afforded colourless crystals (8.04 g, 64%), m.p. 217–220°C, which consisted of *exo*- and *endo*-**10c** (2:3, ^{1}H NMR). Evaporation of the solvent from the mother liquor yielded a yellow oil from which a second crop (1.88 g, 15%, m.p. 218–220°C) was obtained after two recrystallizations from methanol. Recrystallization from methanol eventually yielded pure *endo*-**10c**, m.p. 223–225°C. – MS, *m/z* (%): 516 (0.1) [M$^+$], 501 (7) [M$^+$ – Me], 489 (0.7) [M$^+$ – HCN], 462 (0.4) [M$^+$ – 2 HCN], 426 (1) [M$^+$ – Me$_3$SiOH], 399 (0.3), 336 (0.4), 285 (14), 284 (54), 258 (19), 73 (100).

1,5-Dimethyl-4,8-diphenylbicyclo[3.3.0]octa-2,6-diene-2,6-dicarbonitrile (**11**): A solution of hydrogen fluoride in pyridine (70%, Merck, 2.3 ml, 93 mmol) was cautiously added under N_2 at 0°C to a stirred solution of *exo*- and *endo*-**10c** (2:3, 5.99 g, 11.6 mmol) in phosphorus oxychloride (44 ml, 0.46 mol). Stirring was continued at 25°C for 40 min. Pyridine (114 ml, 1.4 mol) was added dropwise at 0°C, and the mixture was heated to 85°C for 3.5 h. To the cooled, red-brown mixture, dichloromethane (100 ml) was added and, at 0°C, cautiously dilute sulphuric acid (1 M, 175 ml) resulting in the evolution of hydrogen cyanide (**Attention!**). The mixture was extracted with dichloromethane (3 × 200 ml). The solvent was distilled in vacuo from the combined extracts leaving a crystalline residue which was redissolved in dichloromethane (150 ml). The solution was extracted with saturated aqueous solutions of potassium carbonate (100 ml) and sodium chloride (100 ml) and dried with sodium sulphate. Distillation of the solvent in vacuo yielded a pale yellow powder (4.68 g) which was redissolved in dichloromethane (30 ml). The solution was filtered through silica gel (50 g, 32–63 μm) which was eluted with dichloromethane (150 ml). Distillation of the solvent yielded a colourless solid (3.05 g, 78%), m.p. 241–245°C. Recrystallization from acetone afforded colourless crystals, m.p. 245–247°C. – MS, *m/z* (%): 336 (35) [M$^+$], 309 (1) [M$^+$ – HCN], 283 (1), 259 (3) [M$^+$ – Ph], 245 (12), 91 (100). – UV (acetonitrile, Figure 3): λ_{max} [nm] (lg ε): 206 (4.631), 262 (2.823) (sh).

1,5-Dimethyl-4,8-diphenyltricyclo[3.3.0.0^{2,8}]octa-3,6-diene-2,6-dicarbonitrile (**4**): The solvents and the aqueous solutions were carefully degassed in vacuo with ultrasonic irradiation and saturated with argon. All operations were performed under argon. Hexachloroethane (1.42 g, 6.0 mmol) and **11** (673 mg, 2.0 mmol) were dissolved in dry dichloromethane (15 ml) with stirring. Aqueous solutions of tetrabutylammonium hydroxide (40%, 0.3 ml) and sodium hydroxide (50%, 13 ml) were added. The vigorously stirred colourless emulsion turned deep brown within 5 min. Stirring was continued until HPLC indicated complete conversion (1.5 h). After addition of water (30 ml), the layers were separated, and the colourless aqueous layer was extracted with dichloromethane (20 ml). The combined organic layers were extracted with a saturated aqueous solution of potassium dihydrogenphosphate (2 × 20 ml) and water (2 × 20 ml). The distillation of the solvent in vacuo was followed by the vacuum sublimation of the excess of hexachloroethane (2 h, 25°C/10^{-1} Torr). The brown residue was dissolved in dichloromethane (30 ml), and the solution was filtered through silica gel (60 g, 32–63 μm) which was eluted with petroleum ether (b.p. 30–50°C)/ethyl acetate (90:10, 500 ml). The solvent was distilled at 0°C/10^{-1} Torr. From the solution of the red residue in ethyl acetate (6 ml), after 2 d at 20–25°C, red crystals (356 mg, 51%) formed, m.p. 134–136°C (dec.), which were pure as shown by HPLC. The crystals are unchanged after 14 d in the laboratory atmosphere in the dark. The mother liquor contained equal amounts of **4**, **11**, (**12** + **13**), and **16**, besides traces of **17** (HPLC). – MS, *m/z* (%): 334 (65) [M$^+$], 333 (11) [M$^+$ – H], 319 (38) [M$^+$ – Me], 307 (16) [M$^+$ – HCN], 306 (9), 292 (23) [M$^+$ – Me – HCN], 57 (100). – UV (acetonitrile, Figure 3): λ_{max} [nm] (lg ε): 240 (4.224), 287 (4.063), 444 (3.235); λ_{min} [nm] (lg ε): 224 (4.193), 271 (4.033), 356 (2.938).

Reaction of **4** *with Oxygen:* After filtration through silica gel of the dichloromethane solution of **4**, prepared as described above from **11** (2.0 mmol), and concentration to a volume of 50 ml at 0°C/10^{-1} Torr, the clear, red solution was stirred in an open flask in the dark for 3 d at 20–25°C while the conversion was monitored by HPLC. Every day, the solvent was replenished to the original volume. The pale yellow solution was filtered through silica gel (60 g, 32–63 μm) which was eluted with dichloromethane (300 ml). After drying with sodium sulphate and distillation of the solvent in vacuo, the products **16** and **17** were separated by MPLC on silica gel with petroleum ether/ethyl acetate (90:10).

1,5-Dimethyl-4,8-diphenyl-4,8-epidioxybicyclo[3.3.0]octa-2,6-diene-2,6-dicarbonitrile (**16**, t_R = 73 min, 186 mg, 26% based on **11**) was obtained as first fraction. Recrystallization from tetrahydrofuran yielded colourless crystals, m.p. 149–150°C (dec.). – MS, *m/z* (%): 366 (3) [M$^+$], 245 (6), 223 (6), 210 (17), 183 (46), 105 (100) [PhCO$^+$], 77 (47). – UV (acetonitrile, Figure 5): λ_{max} [nm] (lg ε): 246 (3.745) (sh), 266 (3.393) (sh).

2-(1-Cyano-3-oxo-3-phenyl-1-propenyl)-2,3-dimethyl-6-phenyl-2H-pyran-4-carbonitrile (**17**, t_R = 89 min, 84 mg, 11% based on **11**) was obtained as second fraction. Recrystallization from dichloromethane yielded yellow crystals, m.p. 155–157°C (dec.). – ^{13}C NMR ([D]trichloromethane, 100 MHz): δ = 18.0, 22.2 (Me), 123.4, 145.3 (=CH–), 80.5, 96.3, 108.6, 131.2, 151.1 (quart. C), 115.3, 116.3 (C≡N), 125.1, 128.33, 128.59, 128.63 (*o*-CH, *m*-CH), 129.9, 134.5 (*p*-CH), 135.0, 139.5 (*ipso*-C), 190.0 (C=O). – MS, *m/z* (%): 366 (9) [M$^+$], 350 (6) [M$^+$ – Me – H], 223 (11), 210 (31) [M$^+$ – PhCO–CH=C–CN], 184 (11), 183 (91), 105 (100) [PhCO$^+$], 77 (51). – UV (acetonitrile, Figure 5): λ_{max} [nm] (lg ε): 233 (4.381), 339 (4.106); λ_{min} [nm] (lg ε): 218 (4.366), 290 (3.776).

X-Ray Diffraction Analyses were performed from transparent colourless (*endo*-**10c**, **11**, **16**), yellow (**17**), or red (**4**) crystals. The cell parameters were determined on the basis of 22 reflections. The numbers of reflections reported in Table 5 were obtained with Mo-K_α radiation and $2\Theta_{max}$ = 55° (graphite monochromator, Wyckoff scan). Measurements were carried out with the system Nicolet R3m/V. Computations were performed with a computer Micro-Vax II. The programme SHELXTL-PLUS[42] was employed. The structures were solved by direct methods and refined anisotropically by the least-squares method. The weighting scheme for R_w is $1/\sigma^2$. The positions of hydrogen atoms were calculated and included in the refinements with isotropic description[43].

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