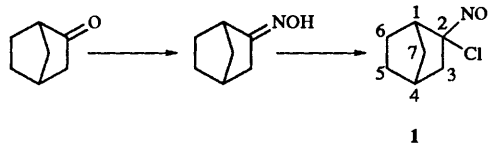
Magnetic resonance studies of the structure and the red photolysis reactions of 2-chloro-2-nitrosonorbornane

Mohamed-Chérif Boucenna,[a] John S. Davidson,[a] Anthony McKee,[a] Andrew L. Porte*,[a] and David C. Apperley[b]

[a] *Department of Chemistry, The University of Glasgow, Glasgow, UK G12 8QQ*
[b] *EPSRC Solid State NMR Service, The University of Durham, Industrial Research Laboratories, South Road, Durham, UK DH1 3LE*

Detailed NMR studies have shown that at 298 K optically-inactive saturated blue solutions of 2-chloro-2-nitrosonorbornane in $CDCl_3$ contain a mixture of the monomeric and dimeric forms of the compound in a ratio of dimer : monomer = 1 : 40 (± 2): this ratio changes with a change in temperature. The analysis assigns the configuration at the >C(2)(NO)(Cl) centre and shows that the monomeric form has the structure (**4**), in which the NO group is on the same side of the molecule as the bridging $>C(7)H_2$ group. White, solid 2-chloro-2-nitrosonorbornane is a 1 : 1 : 1 : 1 mixture of four diastereoisomeric forms of *trans*-diazodioxide (**5**). The white solid readily sublimes at ambient temperature and monomeric vapour forms a blue-green cast on its surface. Red-irradiation of the compound, *in vacuo*, produces white crystals and a viscous brown oil. The white crystals contain norbornan-2-one (**6**), the *syn*- and *anti*-forms of the norbornan-2-one oximes, (**7**) and (**8**), and a lactam, (**9**). These compounds are present in the viscous brown oil which also contains three other compounds to which the structures (**10**), (**11**) and (**12**) are assigned. The reaction mixture is EPR silent. The spectroscopic evidence enables some of the steps in the red photolysis reactions of (**4**) to be unravelled.

2-Chloro-2-nitrosonorbornane, *i.e.* 2-chloro-2-nitrosobicyclo-[2.2.1]heptane (**1**), can be prepared[1] by allowing chlorine to



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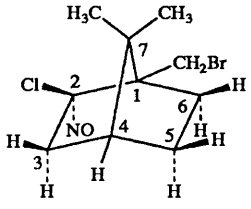
Scheme 1

react with the oxime[2] of norcamphor.[3] Unlike most other geminal chloronitrosobicycloheptanes, compound **1** is a white solid with a blue-green cast on its surface and it melts at *ca.* 44 °C to give a deep-blue liquid. The vapour is lachrymatory. The solid is very volatile and if it is left on a watch-glass it sublimes and disappears within a few hours. It dissolves in most of the common organic solvents to give a deep-blue solution whose cryoscopic properties and visible absorption spectrum show that it is essentially monomeric in benzene and in ethanol.[4] Kayen has reported[5] that 'the chemical shifts of the C-2 carbon atoms in 2-chloro-2-nitrosonorbornane and in its diastereoisomer (with interchanged positions of the geminal isomers) are not identical'.

Single-crystal X-ray analysis reveals[6] that the molecular structure and the configuration at C-2 in (+)-10-bromo-2-chloro-2-nitrosocamphane† are as shown in structure **2**. Careful spectroscopic studies[7] of the action of red light on this solid, and also[8] on solid (−)-2-chloro-2-nitrosocamphane (**3**), involved very detailed applications of magnetic resonance spectroscopy and in the course of that work the following important points emerged. (*i*) In geminal *chloronitroso* derivatives of bicyclo[2.2.1]heptane, ^1H NMR signals from a neighbouring hydrogen nucleus that is *cis* to the chlorine atom appear at lower applied fields, *i.e.* at larger δ-values, than signals from the corresponding hydrogen atom that is *cis* to NO. On



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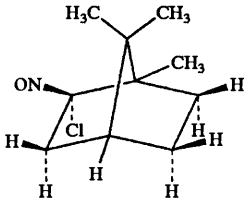

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the other hand, in the corresponding geminal *chloronitro* derivatives it is the signals from the neighbouring hydrogen atom that is *cis* to the NO_2 group that are at lower applied fields, *i.e.* at larger δ-values. Careful analysis of the complicated ^1H NMR spectra of these terpene derivatives enables the configurations at the chiral >C(NO)(Cl) and $>C(NO_2)(Cl)$ centres to be determined and the NMR spectra signify when inversion of configuration takes place during the course of a chemical reaction. (*ii*) The structure of (−)-2-chloro-2-nitroso-camphane is as shown in **3**, *i.e.* its configuration at C-2 is opposite to that in compound **2**. (*iii*) Red-irradiation of the solid forms of compounds **2** and **3** produces several aminoxyl radicals. (*iv*) The spectroscopic studies[7,8] enable some of the solid-state photochemical reaction mechanisms to be unravelled and they identify several interesting rearrangement reactions that take place during the red photolysis.

The synthesis of **1** produces a racemic mixture of the compound and so its solutions are not optically active. Mitchell and his co-workers therefore were not able to extend their Cotton-effect studies[1,9-12] of the geminal chloronitroso derivatives of the terpenes to include 2-chloro-2-nitrosonorbornane and so the configuration at the chiral C-2 centre in the monomeric form of that compound, and the structure(s) of its dimer(s) are undefined. We have therefore used detailed NMR and other spectroscopic methods to determine the structures of the monomeric and dimeric forms of this substance and unravel the mechanisms of some of the reactions that take place when it is irradiated with red light.

† Camphane = bornane.

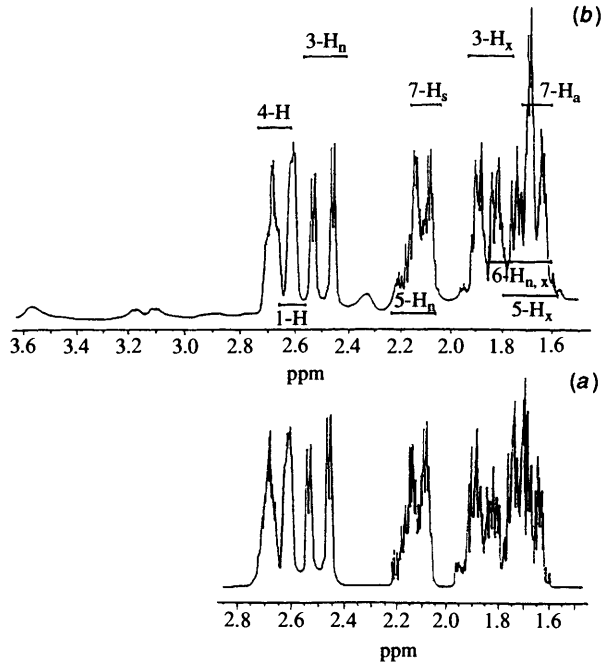


Fig. 1 (*a*) Calculated monomer spectrum and (*b*) the observed 200.132 MHz ^{1}H NMR spectrum of 2-chloro-2-nitrosonorbornane in $CDCl_3$ solution. (*a*) was calculated using chemical shifts and coupling constants listed in Table 1 and Lorentzian lines, half-width at half-height = 1 Hz.

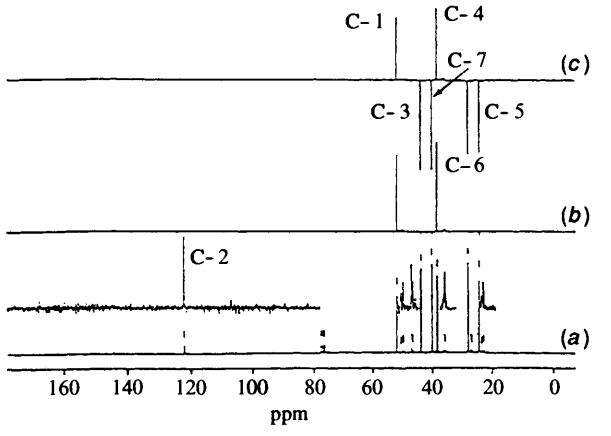


Fig. 2 (*a*) $^{13}C-\{^1H\}$ NMR spectrum and (*b*) the corresponding θ = 90° and (*c*) θ = 135° DEPT spectra of 2-chloro-2-nitrosonorbornane in $CDCl_3$ solution, at ambient temperature

Results and discussion

^{1}H and ^{13}C NMR spectra of 2-chloro-2-nitrosonorbornane

Compound **1** dissolves in $CDCl_3$ to give a deep-blue solution whose ^{1}H, $^{13}C-\{^1H\}$ and $^{13}C-\{^1H\}$ DEPT, 90° and 135°, spectra are shown in Figs. 1(*b*) and 2(*a*)–(*c*), respectively. These spectra enable resonances from C-1, C-2, C-3, C-4 and C-7 to be identified but, because of extensive overlap, they do not by themselves enable the ^{1}H signals to be assigned, nor do they distinguish between signals from C-5 and C-6. However, simultaneous use of these figures and connectivity data obtained from 2D $^{13}C-^1H$ HETCOR and $^1H-^1H$ COSY spectra does enable all ^{13}C and ^{1}H chemical shifts and $^1H-^1H$ coupling constants to be assigned. These are listed in Table 1. Fig. 1(*a*) is a 200.132 MHz ^{1}H NMR spectrum that was calculated from the appropriate spin-Hamiltonian parameters listed in Table 1.

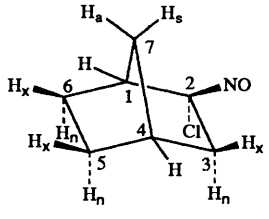
Table 1 ^{1}H and ^{13}C chemical shifts, δ_H and δ_C, and $^1H-^1H$ coupling constants, J_{H-H}, for the monomeric form of 2-chloro-2-nitrosonorbornane in $CDCl_3$

$\delta_H(CDCl_3)$				
1-H	3-H_{endo}	3-H_{exo}	4-H	5-H_{endo}
2.602	2.490	1.849	2.678	2.150
5-H_{exo}	6-H_{endo}	6-H_{exo}	7-H_{syn}	7-H_{anti}
1.697	1.890	1.720	2.113	1.665

$\delta_C(CDCl_3)$						
C-1	C-2	C-3	C-4	C-5	C-6	C-7
51.80	122.10	43.74	38.35	24.17	28.33	40.06

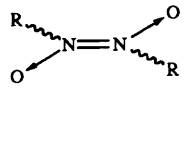
$J_{(H-H)}$/Hz			
1-H, 4-H	1-H, 6-H_{exo}	1-H, 6-H_{endo}	1-H, 7-H_s
2.0	4.3	1.5	2.0
1-H, 7-H_a	3-H_{exo}, 3-H_{endo}	3-H_{exo}, 4-H	3-H_{exo}, 5-H_{exo}
2.0	14.0	4.3	2.0
3-H_{endo}, 4-H	3-H_{endo}, 7-H_a	4-H, 5-H_{exo}	4-H, 5-H_{endo}
0.0	2.8	4.3	1.5
4-H, 7-H_s	4-H, 7-H_a	5-H_{exo}, 5-H_{endo}	5-H_{exo}, 6-H_{exo}
2.0	2.0	10.5	9.1
5-H_{exo}, 6-H_{endo}	5-H_{endo}, 6-H_{exo}	5-H_{endo}, 6-H_{endo}	5-H_{endo}, 7-H_s
4.0	4.0	9.1	2.6
6-H_{exo}, 6-H_{endo}	6-H_{endo}, 7-H_s	7-H_s, 7-H_a	
10.5	2.6	10.0	

The intense peak observed at 1570 cm^{-1} in the IR absorption spectrum of 2-chloro-2-nitrosonorbornane in chloroform, characteristic[13,14] of the N=O stretching vibration of a C-nitroso monomer, the sharp peaks in Figs. 1(*b*) and 2(*a*)–(*c*), the analyses and the data listed in Table 1 all establish that the major species present in $CDCl_3$ solution is the monomeric form of 2-chloro-2-nitrosonorbornane. Furthermore, ^{1}H NMR signals from 3-H_{endo} lie at lower applied fields than signals from 3-H_{exo}. Hence, 3-H_{endo} is *cis* to the chlorine atom[7,8] and the structure of the monomer is as shown in **4**. The NO residue



$H_n = H_{endo}$ $H_s = H_{syn}$
$H_x = H_{exo}$ $H_a = H_{anti}$

4



[R–NO = 4]

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on C-2 is on the same side as the bridging >C(7)H_2 group. The configuration at C-2 is the same as in (−)-2-chloro-2-nitrosocamphane (**3**) opposite to the corresponding configuration in (+)-10-bromo-2-chloro-2-nitrosocamphane (**2**) and the chloroform solution of 2-chloro-2-nitrosonorbornane contains equal amounts of the *R*- and *S*-enantiomers of structure **4**.

Figs. 1(*b*) and 2 also reveal the presence of small amounts of other species in the $CDCl_3$ solution that give rise to additional broad ^{1}H signals in Fig. 1(*b*) and to extra weak ^{13}C signals in Fig. 2(*a*). These signals arise from diastereoisomers of the dimeric form **5** and their ^{13}C chemical shifts are listed in Table 2. Fig. 3 is the $^{13}C-\{^1H\}$ NMR spectrum of the same $CDCl_3$ solution recorded at 263 K. At this lower temperature the equilibrium Dimer $\rightleftharpoons$ 2 [Monomer] shifts markedly to the left and a far clearer spectrum of the dimer is then obtained. If, however, the temperature of the solution is raised to 333 K then the dimer's contribution to the ^{13}C NMR spectrum almost

Table 2 ^{13}C chemical shifts, δ, for the dimeric form of 2-chloro-2-nitrosonorbornane (**5**) in the pure solid and in saturated $CDCl_3$ solution at 263 K

	C-1	C-2	C-3	C-4	C-5	C-6	C-7
Pure solid	50.43	104.36 98.02	47.48	36.77	24.24	26.93	39.22
In $CDCl_3$	50.25 49.77 49.70	99.23 98.78	46.75 46.47	35.74	22.77	26.85	38.43

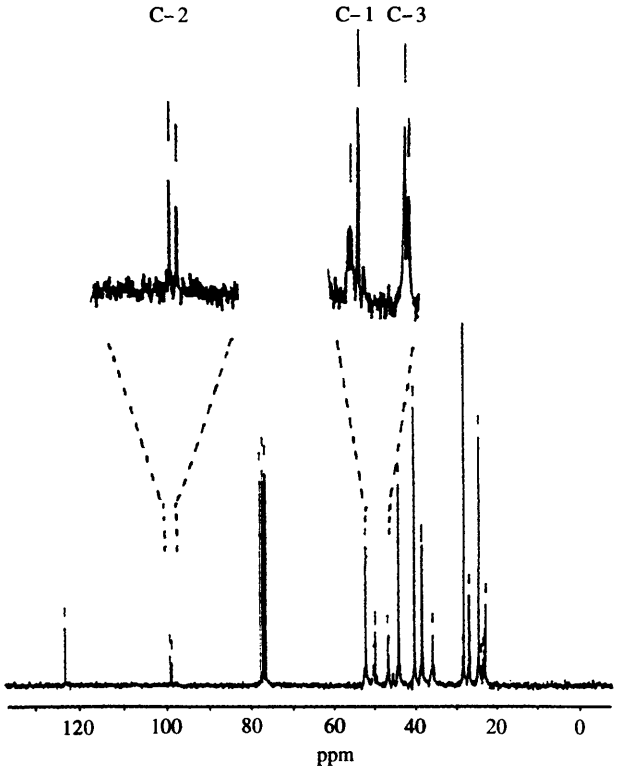


Fig. 3 $^{13}C-\{^1H\}$ NMR spectrum of a saturated solution of 2-chloro-2-nitrosonorbornane in $CDCl_3$ solution, at 263 K. The inserts are expanded signals from ^{13}C-1, ^{13}C-2 and ^{13}C-3 nuclei in the dimeric form, structure **5**, of this compound.

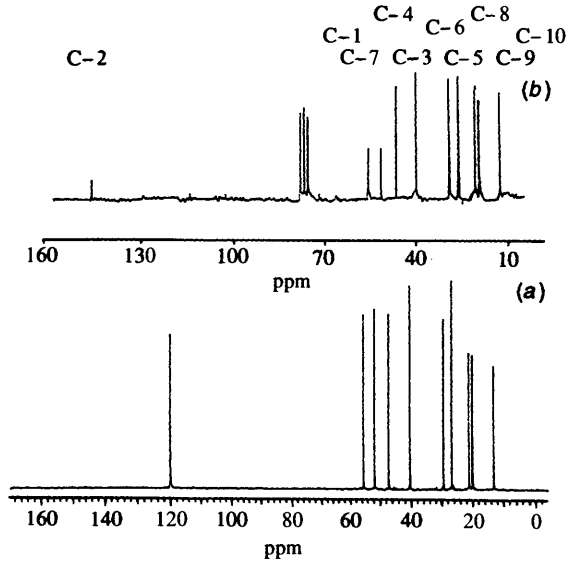


Fig. 4 (*a*) ^{13}C CP MAS spectrum of solid (−)-2-chloro-2-nitrosocamphane at ambient temperature and (*b*) the $^{13}C-\{^1H\}$ NMR spectrum of its solution in $CDCl_3$

disappears. These changes are fully reversible. Similar reversible changes are also observed when the corresponding ^1H NMR spectra are examined over the same range of temperature.

A $^{13}C-\{^1H\}$ CP MAS spectrum of the deep-blue solid form of (−)-2-chloro-2-nitrosocamphane (**3**) and a $^{13}C-\{^1H\}$ spectrum of its solution in $CDCl_3$ are shown in Figs. 4(*a*) and (*b*), respectively. Solution and solid-state ^{13}C chemical shifts are listed in Table 3. The two sharp spectra and the data in Table 3 show that, as in other camphane derivatives,[15] the almost-spherical molecules of compound **3** rotate rapidly and randomly inside the solid at ambient temperature. However these molecules cannot be rotating independently of each other, for the ^{13}C shifts in the solid are almost the same as in solution, except for the C-2 signals which show an unusually large solid-state shift of almost 25 ppm. The C-2 environment in the solid must therefore differ from that in solution. The solution shift, 145.04 ppm, is very similar[7,8] to the corresponding shift, 145.71 ppm, observed for C-2 in a $CDCl_3$ solution of compound **2**, and it appears to be typical of 2-chloro-2-nitrosocamphanes. The C-2 shift in the solid form of compound **3**, 120.20 ppm, might imply, first, that in its crystal structure, molecules are packed together in pairs so that C-2 in one molecule lies close to the C(2)(NO)(Cl) residue of its paired, structurally related molecule, secondly, that these paired molecules retain their mutual orientations inside the solid and, thirdly, that it is these structurally related pairs of molecules that rapidly and randomly rotate, as a unit, inside the solid at ambient temperature. The C-2 ^{13}C chemical shifts of compounds **2** and **3**, in $CDCl_3$ solution, are themselves anomalous since shifts of +112.1 and +112.6 ppm are observed[7,8,16] in their corresponding chloronitro analogues. C-nitroso shifts are normally 6–11 ppm more deshielded than the corresponding C-nitro signals, so the C-2 solution chemical shifts for compounds **2** and **3** were expected to fall within the range $118 \leqslant \delta \leqslant 124$, rather than at the observed δ +145. The origin of the additional observed paramagnetic shift of 20–25 ppm is not known. It implies that the electron distributions in the neighbourhood of the *gem*-chloronitroso residues are unusually distorted in the chloronitrosocamphanes, possibly as a result of steric overcrowding at the nitroso residues in these molecules.

The 75.431 MHz ^{13}C CP MAS spectrum of dimeric solid 2-chloro-2-nitrosonorbornane at ambient temperature, Fig. 5, is typical of that obtained from a solid in which internal motions are restricted.[15] Chemical shifts of ^{13}C-1 and ^{13}C-3–^{13}C-7 obtained from this spectrum are very similar to the corresponding shifts obtained from the less intense peaks in the $CDCl_3$ solution spectrum shown in Figs. 2 and 3, and listed in Table 2, but the $\delta \approx 122$ signal from the ^{13}C nucleus of the monomeric >C(2)(NO)(Cl) residue has, in the solid, shifted upfield to become an asymmetric multiplet at *ca.* 100 ppm on dimerisation to $C(Cl)N_2O_2(Cl)C$. The broad multiplet arises from the effects of residual second-order direct magnetic dipolar perturbations that are transferred to the ^{13}C-2 nucleus, by the neighbouring quadrupolar ^{14}N and $^{35/37}Cl$ nuclei; magic angle spinning of solids does not completely average out magnetic

Table 3 ^{13}C chemical shifts, δ for (−)-2-chloro-2-nitrosocamphane (**3**) in the pure solid and in $CDCl_3$ solution

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
Pure solid	55.64	120.20	40.61	47.35	26.98	29.73	51.93	21.24	20.07	13.15
In $CDCl_3$	55.47	145.04	40.31	46.75	26.45	29.46	51.47	20.73	19.40	12.68

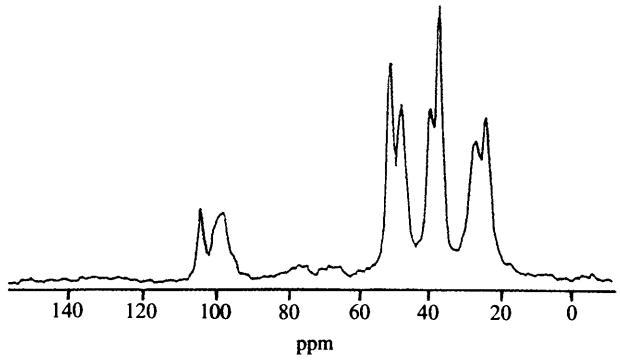


Fig. 5 75.431 MHz ^{13}C CP MAS spectrum of solid 2-chloro-2-nitrosonorbornane at ambient temperature

dipolar couplings that involve ^{13}C nuclei directly bonded to quadrupolar nuclei.[17,18] Only one broadened signal is obtained from each of ^{13}C-4, ^{13}C-5, ^{13}C-6 and ^{13}C-7 in the weak peaks observed in the $CDCl_3$ solution spectrum in Fig. 3, but ^{13}C-1, ^{13}C-2 and ^{13}C-3 each give rise to pairs of weak signals. IR absorption peaks at 1570 or at 1420 and 1323–1344 cm^{-1}, characteristic of monomeric N=O and *cis*-diazodioxide vibrations, respectively, are not present in the IR absorption spectrum of the dimeric solid 2-chloro-2-nitrosonorbornane, but an absorption at 1182 cm^{-1}, characteristic of a *trans*-diazodioxide,[19–21] is observed. A 30.405 MHz ^{15}N CP MAS spectrum of the solid shows only one peak, at −67.232 ppm relative to the nitrate signal in ammonium nitrate, a peak that is very different from the paramagnetic deshielded shifts of $+500 \leqslant \delta \leqslant 600$ that are typical[22,23] of C-nitroso groups. It lies within the ^{15}N shift range assigned[22,23] to azoxy, R–N=N(O)R, residues.

The spectroscopic evidence shows that there are no other geometric isomers of structure **4** in this substance, that the solid has the *trans*-diazodioxide structure (**5**), and that the solution and solid are racemic mixtures containing equal amounts of the *RR*, *SS*, *RS* and *SR* dimeric forms of optical isomers of the monomer **4**. NMR spectra of the *RS* and *SR* forms are the same. The NMR spectra of the *RR* and *SS* forms are nearly, but not quite, identical and the presence of equal amounts of these two groups of isomers explains the intensity patterns that are observed in the C-1, C-2 and C-3 contributions to the weak components of the ^{13}C–$\{^1H\}$ spectrum shown in Fig. 3.

Measurement of the relative areas of the appropriate regions in the ^1H NMR spectra show that in saturated deuteriochloroform solution, at 298 and 263 K, the relative concentrations of the different forms of 2-chloro-2-nitrosonorbornane are as given in Table 4.

Table 4 Relative concentrations of the two forms of 2-chloro-2-nitrosonorbornane

T/K	[Dimer]:[Monomer]
298	1:40 (± 2)
263	1:20 (± 2)

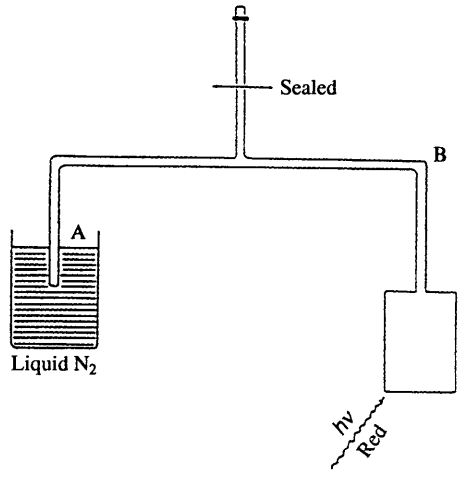


Fig. 6

Red photolysis reactions of 2-chloro-2-nitrosonorbornane

A sample of the dimeric solid 2-chloro-2-nitrosonorbornane was placed in limb B of the apparatus shown in Fig. 6, which was then evacuated and sealed, and the compound was then exhaustively irradiated at 290 K with red light. During the irradiation, limb A was cooled in liquid nitrogen. Dimeric solid 2-chloro-2-nitrosonorbornane is white and it does not absorb visible light, but the blue–green cast on its surface implies the presence of monomeric vapour and it is this that is photolysed by the red light.

During photolysis, liquid products are formed. These dissolve the parent dimer and on red irradiation the blue–green cast on the surface of the solid changes to a blue colour, after which the substance becomes a deep-blue liquid, which on exhaustive irradiation *in vacuo* then slowly changes to become a brown viscous oil. During irradiation, white crystals form on the inside wall at bend B of the reaction vessel and since they grow at a site remote from the original starting material, it is believed that these crystals are formed by photochemical reactions of the monomer in the vapour. Despite a number of attempts, using several procedures, we have not managed to satisfactorily separate the components in these crystals, but the pure components have been identified by NMR methods.

$\theta = 90°$ and $\theta = 135°$ ^{13}C–$\{^1H\}$ DEPT spectra of a $CDCl_3$ solution of these white crystals turn out to be particularly interesting. They are shown in Fig. 7. Only >CH methine residues contribute to the $\theta = 90°$ DEPT spectrum. The eight >CH peaks in Fig. 7(*b*) immediately indicate that these crystals contain four major components that possess the bicyclo[2.2.1]-heptane structure and their relative intensities enable the pairs of >CH residues to be connected. The relative amounts of the four components can also be obtained from Fig. 7(*b*). Similar analysis of the $\theta = 135°$ DEPT spectrum in Fig. 7(*c*) then enables connections within the methylene $>CH_2$ residues to be made and the four components in the white crystals can be identified. They are norbornan-2-one[24] (**6**, 10% abundance), the norcamphor oximes[24] (**7**) and (**8**), the isomers in which –OH is *syn* and *anti* with respect to C-3 being present in 50% and 10% abundances, respectively, and one lactam, present in 30% abundance, whose ^{13}C chemical shifts are consistent with the structure **9**. Detailed assignments of the NMR data are given in Table 5.

The IR and mass spectra of the white crystals support the

Table 5 ^{13}C chemical shifts, δ, of the components of the white crystalline photolysis products, in $CDCl_3$ solution

	C-1	C-2	C-3	C-4	C-5	C-6	C-7
Norbornan-2-one (**6**)	49.83	218.9	45.23	35.28	27.14	24.15	37.59
Norcamphor oxime (**7**)	42.63	178.60	34.84	34.89	26.00	26.55	39.73
Norcamphor oxime (**8**)	41.65	178.00	37.66	35.77	25.12	26.55	38.49
Lactam (**9**)	53.87	175.27	37.04	31.12	29.04	35.19	39.73

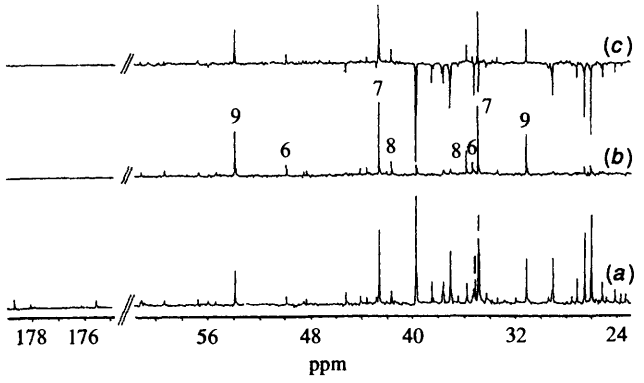


Fig. 7 (*a*) $^{13}C-\{^1H\}$ NMR spectrum and (*b*) the corresponding $\theta = 90°$ and (*c*) $\theta = 135°$ DEPT spectra of the white crystals in $CDCl_3$ solution

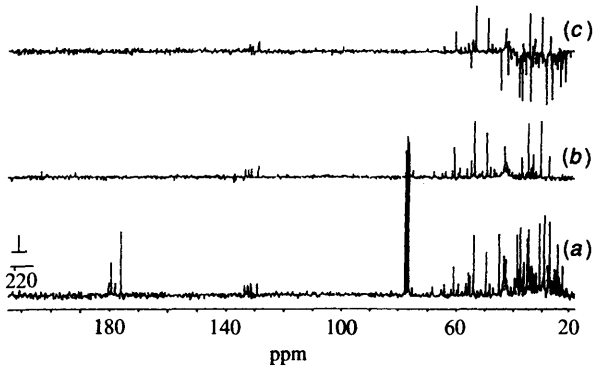
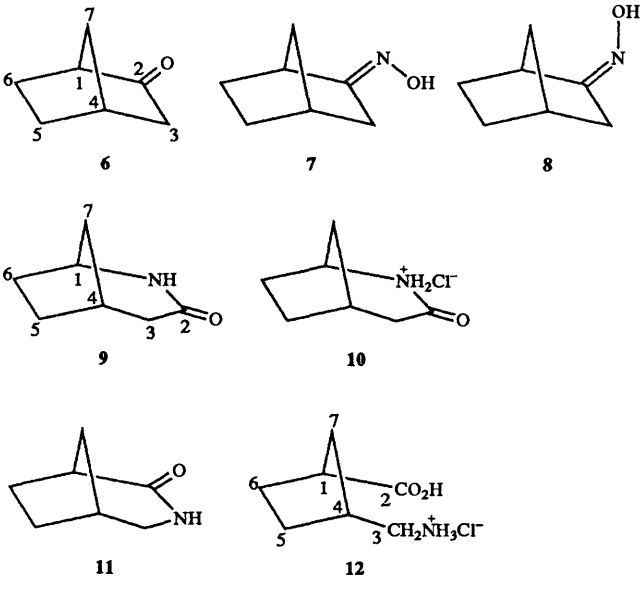


Fig. 8 (*a*) $^{13}C-\{^1H\}$ NMR spectrum and (*b*) the corresponding $\theta = 90°$ and (*c*) $\theta = 135°$ DEPT spectra of the brown viscous oil in $CDCl_3$ solution



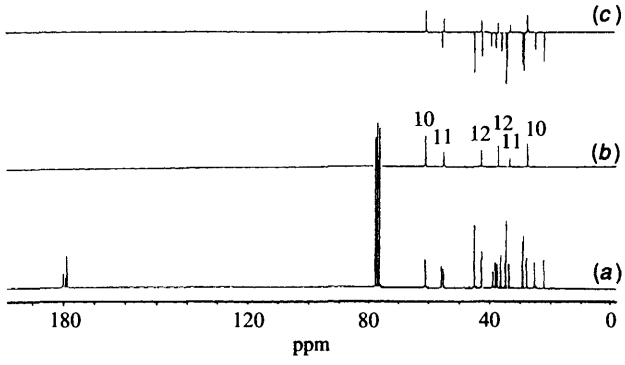


Fig. 9 (*a*) The more intense peaks in the $^{13}C-\{^1H\}$ NMR spectrum and (*b*) the corresponding $\theta = 90°$ and (*c*) $\theta = 135°$ DEPT spectra of the brown viscous oil in $CDCl_3$ solution, after subtraction of the spectra of compound **6**, **7**, **8** and **9**

NMR analysis and they show that the protonated form of the lactam is also present in the crystals. The protonated form is not detected in the NMR or IR spectra of the $CDCl_3$ solutions.

Similar methods were used to identify the compounds present in the solution that is obtained when the residual brown viscous oil is dissolved in deuteriochloroform. Its $^{13}C-\{^1H\}$ 90° and 135° DEPT spectra are shown in Fig. 8. Matching of pairs of the most intense methine >CH– signals in Fig. 8(*b*) reveals the presence of at least seven compounds in the brown viscous oil, including the four components in the white crystals, although their relative abundances in the oil are not in the same ratios already identified in the crystals. In the oil the relative ratios of norbornanone (**6**), oximes (**7**) and (**8**) and lactam (**9**) are **6**:**7**:**8**:**9** = 35:10:5:20%.

Fig. 9 shows the more intense ^{13}C signals of Fig. 8 that remain after the spectra of compounds **6**, **7**, **8** and **9** have been subtracted. It reveals the presence of three more compounds in the brown oil which, on the basis of their ^{13}C chemical shifts are assigned structures **10**, **11** and **12**, with relative concentrations of 3:1:2, respectively. Their ^{13}C chemical shifts are listed in Table 6.

The IR and mass spectra of the oil are consistent with the NMR analysis.

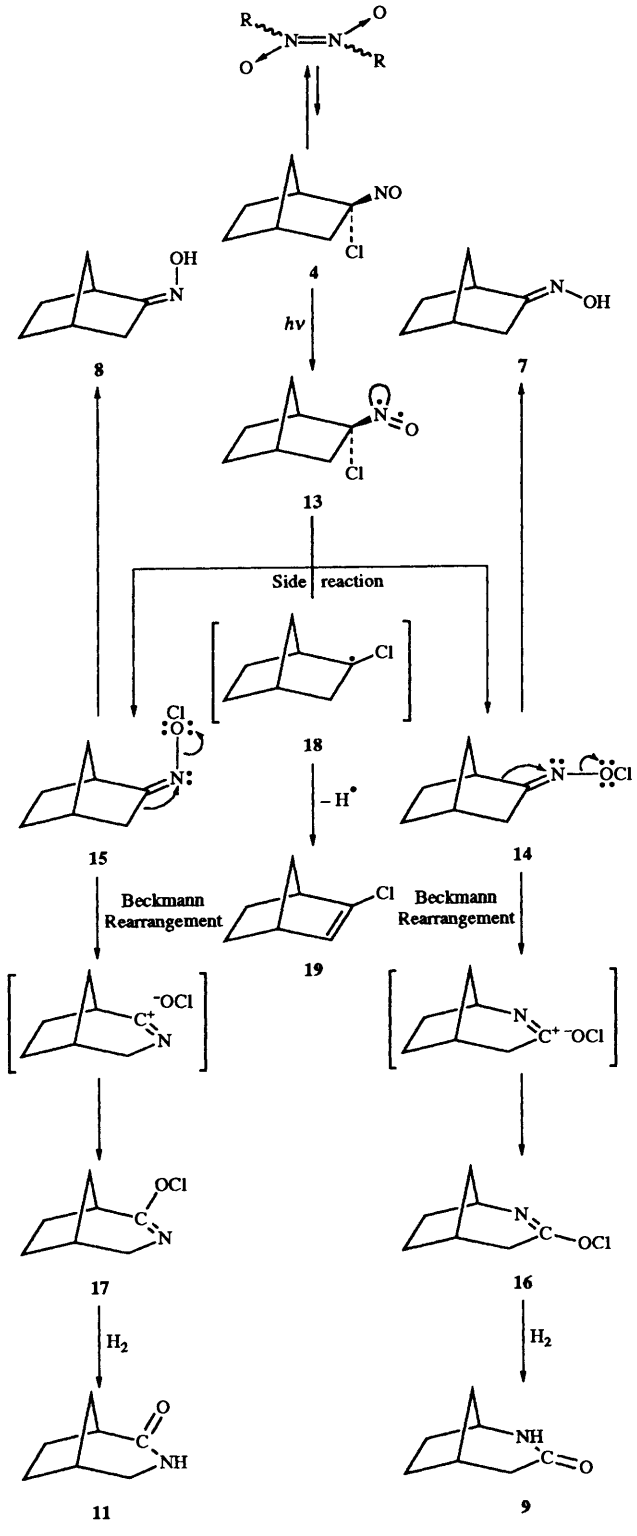
Attempts to detect EPR spectra of aminoxyl radicals formed during the red irradiation of 2-chloro-2-nitrosonorbornane were not successful. At all times the reaction mixture appears to be EPR silent and in that respect the photolysis of this compound differs markedly from the photolysis reactions that are encountered in solid C-nitroso derivatives.[7,8,14,25-29]

Photolysis reaction mechanisms

The experimental results enable mechanisms to be constructed for the photochemical reactions that take place when 2-chloro-2-nitrosonorbornane is irradiated with red light. The sequence of reactions is summarized in Scheme 2. The initial red-irradiation of the solid, in equilibrium with its vapour, photolyses the monomeric vapour and liquid products are formed.

Table 6 ^{13}C chemical shifts of the additional photolysis components, compounds **10**, **11** and **12**, in the brown viscous oil, in $CDCl_3$ solution

	C-1	C-2	C-3	C-4	C-5	C-6	C-7
Lactam hydrochloride (**10**)	60.85	179.86	44.90	27.52	22.11	28.84	34.44
Lactam (**11**)	55.00	178.98	38.86	33.52	29.03	36.10	37.45
Amino acid hydrochloride (**12**)	42.68	179.17	55.57	37.33	25.01	34.63	42.48



Scheme 2

The equilibrium then shifts to produce more monomeric vapour, and this in its turn is photolysed by the red light. The NO group in **4** undergoes a $^1\pi^* \leftarrow {}^1n$ (nitrogen) transition and the intermediate **13** forms. This rearranges to the isomeric chloro oximes (**14**) and (**15**). At this stage, these chloro oximes either lead to the oximes (**7**) and (**8**), respectively, as hydrogen atoms are made available *via* the side reaction shown in Scheme 2, or alternatively **14** and **15**, triggered by the inductive effect of the Cl atom undergo Beckmann-like rearrangements to give **16** and **17**, respectively. These, in their turn, further react to give **9** and **11**, respectively, and thence compounds **10** and **12**.

Although the scheme is speculative it should be noted that similar Beckmann-like rearrangements have been invoked to account for the reaction products that are obtained when aluminium chloride, or Me_2AlCl or Me_3Al, react with geminal chloronitroso derivatives of other terpenes,[30–32] and when solid (−)-2-chloro-2-nitrosocamphane is red irradiated.[8] The lactams **9** and **11** are also obtained in the Beckmann rearrangement of norcamphor oxime.[33,34] Scheme 2 accounts for the formation of the main photolysis products identified in this work and it explains why the EPR spectra of aminoxyl radicals are not detected in this case if, in the vapour, radical **18** loses a hydrogen atom before it gets time to collide with another parent molecule (**4**) to form a bisalkyl aminoxyl radial.[8] Cage effects in solid (−)-2-chloro-2-nitrosocamphane enable the camphane analogues of **16**, **17**, **9** and **11** to react further with a ClO^- ion or a $ClO^•$ radical and form an acyl aminoxyl.[8] Additional collisions of this kind are unlikely to take place in the vapour phase of 2-chloro-2-nitrosonorbornane at low pressure and therefore further oxidation to the corresponding acyl aminoxyl radicals is not observed.

Experimental

NMR Measurements

^{13}C and ^{15}N CP MAS spectra of solids were recorded on a Varian VXR 300 spectrometer using the following conditions.

^{13}C Measurements. Frequency = 75.431 MHz; spin rate = 3320 Hz; spectral width = 20 000 Hz; acquisition time = 19.2 ms; relaxation delay = 10.0 s; 90° pulse; 1000 scans; cross polarization with flip-back contact time of 1 ms.

^{15}N Measurements. Frequency = 30.405 MHz; spin rate = 2900 Hz; spectral width = 30 030 Hz; acquisition time = 19.2 ms; relaxation delay = 10.0 s; 90° pulse; 8512 scans; cross polarization with flip-back contact time of 2 ms.

Standard ^1H, ^{13}C–$\{^1H\}$ and DEPT ^{13}C spectra of saturated $CDCl_3$ solutions were recorded on a Bruker AM 200 SY spectrometer, with the following settings.

^1H Measurements. Frequency = 200.132 MHz; spectral width = 4000 Hz; relaxation delay = 1 s; acquisition time = 2.05 s; 35° pulse; 64 scans.

^{13}C–$\{^1H\}$ and ^{13}C DEPT Measurements. ^{13}C Frequency = 50.323 MHz; spectral width = 12 500 Hz; relaxation delay = 0 s; acquisition time = 0.655 s; 35° pulse; 8000 scans. The DEPT spectra were recorded using similar parameters with a DEPT delay time τ, $[2J(^{13}C, {}^1H)]^{-1}$, of 3.4 ms; 3840 scans.

The high resolution ^1H NMR spectrum shown in Fig. 1(*a*) was built up out of segments calculated by standard techniques[35] that were programmed for a SALFORD FORTRAN 77 version of the program UEA NMR BASIC, combined with GHOST 80 graphics routines, for the University of Glasgow's ICL 3980 mainframe computer. The transitions were assumed

to give rise to Lorentzian absorption lines, half-width at half-height 1 Hz.

Synthesis of the dimer of 2-chloro-2-nitrosobicyclo[2.2.1]-heptane (5)

The norcamphor, *i.e.* bicyclo[2.2.1]heptan-2-one, shown in Scheme 1, was prepared by using the method described by Alder and Rickert to oxidize α-norborneol,[3] and it was then converted into its oxime,[2] bp = 80–90 °C/1.5 mmHg. Solutions of compound **5** are decomposed by light. This compound must be prepared and handled in subdued blue light.

Norcamphor oxime (8.2 g) was dissolved in dry diethyl ether (120 cm^3) and cooled in ice. Chlorine gas was passed through the solution until the blue colour that developed turned emerald green and the diethyl ether was then evaporated off in a stream of nitrogen. The remaining solid (*ca.* 10 g) was washed thoroughly with light petroleum (bp 40–60 °C) and purified by chromatography, on a column of H alumina, to give 6.0 g (57%) of white dimer (**5**) (Found: C, 52.6; H, 6.3; Cl, 22.3; N, 8.7. $[C_7H_{10}ClNO]_2$ requires C, 52.64; H, 6.32; Cl, 22.25; N, 8.77%). The white solid melts, mp *ca.* 44 °C, to give a deep blue liquid. It dissolves in all the common organic solvents to give deep-blue solutions. In ethanol $\varepsilon_{max} = 25$, $\lambda_{max} = 6500$ Å when $c = 0.031$ mol dm^{-3}. ^1H and ^{13}C NMR data in Table 1. ν_{max}(KBr)/cm^{-1} 3040, 3001 [C(1)H, C(4)H], 2979, 2958, 2938, 2936 [C(3)H_2, C(5)H_2, C(6)H_2 and C(7)H_2 asymmetric stretching modes], 2925, 2920, 2880, 2738 [C(3)H_2, C(5)H_2, C(6)H_2 and C(7)H_2 symmetric stretching modes], 1472, 1452, 1442 [C(3)H_2, C(5)H_2, C(6)H_2 and C(7)H_2 deformation modes], 1320, 1302, 1288 [C(3)H_2, C(5)H_2, C(6)H_2 and C(7)H_2 wag vibrations], 1182 [*trans*-dimer N–O stretching vibration], 800 [dimer C–N–O skeletal bending mode] and 763 [C–Cl stretching vibration]. Electron impact mass spectrum; *m/z* 131.0 ($[C_7H_{10}{}^{37}Cl]^+$ 7.95%), 129.0 ($[C_7H_{10}{}^{35}Cl]^+$ 23.86), 94.1 ($[C_7H_{10}]^+$ 10.23), 93.1 ($[C_7H_9]^+$ 100.00), 91.0 ($[C_7H_7]^+$ 29.55), 77.1 ($[C_6H_5]^+$ 30.68), 67.1 ($[C_5H_7]^+$ 36.36), 65.2 ($[C_5H_5]^+$ 22.73) and 41.0 ($[C_3H_5]^+$ 13.64). Parent peaks for $[C_7H_{10}ClNO]_2$ or for $C_7H_{10}ClNO$ are not observed since the NO groups are cleaved in the mass spectrometer.

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