Single-crystal Electron Paramagnetic Resonance Studies of the Action of Red Light on the Needle Form of Humulene Nitrosite,† $C_{15}H_{24}N_2O_3$: the First Nitroxide Radical Formed in the Photochemical Reaction

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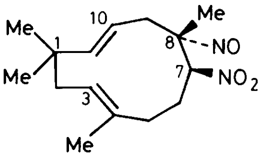
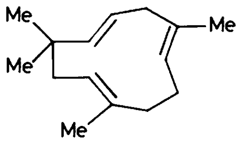
Spin-Hamiltonian parameters, in an arbitrarily chosen crystal *xyz* frame, have been extracted from e.p.r. spectra of the first nitroxide radical that is obtained when a single crystal of the needle form of humulene nitrosite (**1**) is briefly irradiated with red light. Diagonalization of the spin-Hamiltonian matrices, followed by transformation into the *abc* frame of the monoclinic unit cell, shows that this first radical is a monoalkyl nitroxide H(R)N$\doteq$O, compound (**7**). The anisotropic components of the magnetic parameters show that this radical undergoes marked thermal motion in the crystal, so that the crystallographically distinguishable molecules in this solid can not be distinguished by e.p.r. methods at 290 K.

Humulene nitrosite (**1**) was first prepared almost a hundred years ago by Chapman,[1,2] and for many years it was used to characterize humulene (**2**), one of the main sesquiterpenes found in the higher boiling fractions of hop oil. Humulene nitrosite can be obtained in one or other of two crystalline forms.[3] Needles are obtained when it is rapidly recrystallized from ethanol, but if the recrystallization from ethanol is allowed to take place slowly, then platelets are also formed. The two forms are deep blue, the colours originating in the intense $\pi^* \longleftarrow n$ transition of the nitroso group at *ca.* 670 nm. They have almost identical spectroscopic properties, and they have been shown[4,5] to be the two lowest-energy forms, of the four possible conformational isomers obtained by rotation of the C(3),‡ C(4) and C(10), C(11) segments through the cycloundecadiene ring. The molecular conformation in the needle form[4] is shown in Figure 1. The corresponding conformation in the platelet form[5] is obtained by rotating the double-bond segments C(3)=C(4) and C(10)=C(11) in this figure, through 180°.



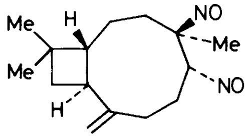
(**1**)



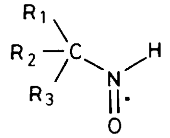
(**2**)

If either form of solid humulene nitrosite is irradiated with red light, then the deep-blue colour is bleached, photolysis takes place, nitrogen, nitric oxide and nitrogen dioxide are evolved, and eventually white solids and a viscous yellow liquid are obtained.[3] A number of diamagnetic products and several nitroxide radicals are produced in the photochemical reactions; the order in which they appear, and their relative abundances, depends on the length of time for which the solid is irradiated.[3]

Solid caryophyllene nitrosite (**3**) undergoes similar red photolysis reactions that have been examined in great detail, and single-crystal e.p.r. studies have shown that, in that particular system, a monoalkyl nitroxide (**4**) is the first nitroxide radical to be formed on irradiation of the solid.[6] Molecular structure and packing in the crystals, and several steps in the red photolyses are very similar for both solids (**1**) and (**3**).[3,4,6]



(**3**)



(**4**)

The earlier studies of the red photochemistry of solid humulene nitrosite were performed on polycrystalline samples,[3] and comparison of the results of that work with those obtained for the more recent single-crystal e.p.r. spectroscopic studies of irradiated caryophyllene nitrosite,[6] led us to believe that at least one nitroxide radical, which is formed during the early stages of the red photolysis of humulene nitrosite, had been missed, and that the compounds we had detected and characterized in the polycrystalline studies are in fact products formed later on in the sequence of photochemical reactions. Furthermore, the earlier polycrystalline e.p.r. spectroscopic work on humulene nitrosite also showed that several nitroxide radicals are formed, and in

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† 2,6,6,9-Tetramethyl-1-nitro-2-nitrosocycloundeca-4,8-diene.

‡ Non-systematic numbering is used here to enable direct comparison with the crystallographic numbering.

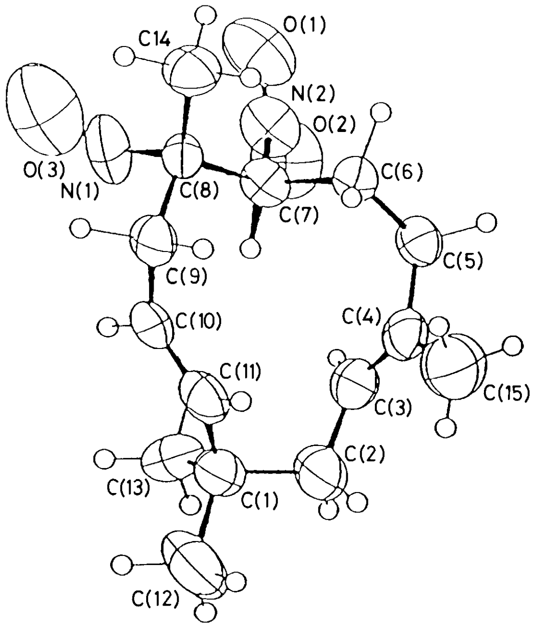


Figure 1. The molecular conformation in the needle form of humulene nitrosite.

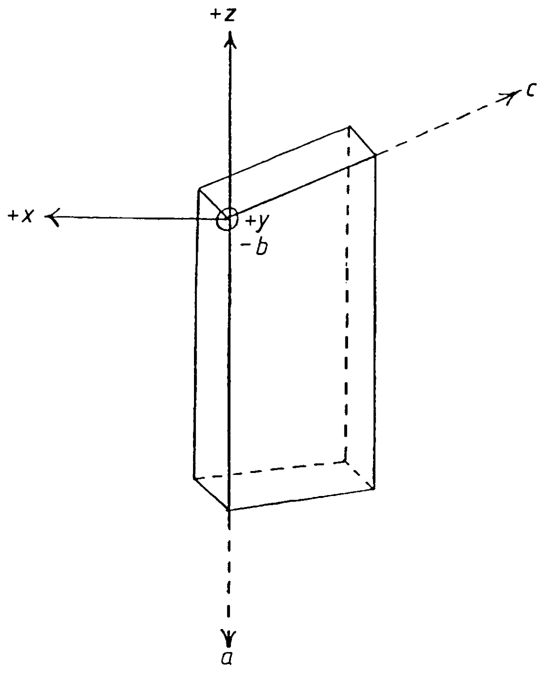


Figure 2. The orthogonal *xyz* frame, and the monoclinic *abc* frame.

some of these, the unpaired electron is coupled to more than one magnetic nucleus; in such circumstances it is notoriously difficult to obtain exact and unambiguous spin-Hamiltonian parameters, since the principal axes of the various tensors do not then always coincide. Precise and detailed information about the magnetic properties, and orientations within the unit cell, of the radicals that are formed in the early stages is important for the understanding of the photochemical reactions in these solids, and so in the present work we have carried out single crystal e.p.r. spectroscopic studies on the needle form of humulene nitrosite subjected to a brief period of irradiation with red light.

Results and Discussion

Humulene was separated from the fraction b.p. 99–100 °C (at 1 mmHg) obtained by redistillation of a sample of the higher-boiling fractions of hop oil, and was then used to synthesize humulene nitrosite.[7] Blue needles of (**1**) were obtained from a saturated solution in ethanol kept at 70 °C in the dark for *ca.* 1 h. The right-handed orthogonal co-ordinate framework, *xyz*, shown in Figure 2, was identified in a well-formed needle, and the crystal was then mounted along its $+z$-axis inside a standard TE_{102} rectangular cavity of a Decca e.p.r. spectrometer. An intense beam of white light from a quartz–halogen lamp was passed through a red filter, and then focused by a double convex lens on to the blue humulene nitrosite crystal, on each of its four main faces in turn for 10 min. The crystal was then orientated so that the magnetic field of the spectrometer lay along the $+x$ direction and the e.p.r. spectrum was recorded, at 290 K, using a microwave frequency of 9 270 MHz. The spectrum was then recorded, with the magnetic field still in the *xy*-plane, at angles, θ, of 15, 30, 45°, – – – –, 210° to the *x* axis. The same needle crystal was then remounted along its $+x$ axis and then along its $+y$ axis, and the e.p.r. spectra were recorded with the magnetic field lying in several orientations in the *yz*- and *zx*-planes, respectively. Some of the single crystal spectra obtained in this way are shown in Figure 3.

The needle form of humulene nitrosite belongs to the monoclinic system, $a = 6.484(2)$, $b = 18.139(8)$, $c = 14.294(3)$ Å, $\beta = 101.33(2)°$, $Z = 4$, space group $P2_1/n$.[4] *X*-Ray rotation and Weissenberg photographs of the same crystal used in the e.p.r. work showed that the *xyz* frame and the monoclinic *abc* frame are related by the transformations

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & 0 & -\sin\beta \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

The four molecules in the unit cell in this crystal form two centrosymmetrically related pairs, the first of which is related to the second by means of a glide plane parallel to the *ac* plane of the cell, so that two sets of equally intense e.p.r. spectra are expected to be obtained for each chemically distinguishable radical that is formed by red irradiation, except when the magnetic field lies along the monoclinic *b*-axis, or in the *ac*-plane, when the symmetry properties of the space-group require that the two spectra be superimposed.

In this work two overlapping spectra were observed consistently, but the first of these was very much more intense than the second, which formed a much weaker background spectrum, and was not related to the first. The expected doubling of the e.p.r. spectrum for an arbitrary orientation of the applied magnetic field was not observed which could indicate one of three possibilities. (*a*) One partner of one centrosymmetrically related pair of humulene nitrosite molecules in the photochemical reaction reacts with one partner from the second pair generated by the glide operation. (*b*) by chance the frames of the tensors in the spin-Hamiltonians of the crystallographically distinguishable radicals in this solid happen to have one principal direction orientated along the monoclinic *b*-axis and the other two principal directions in the monoclinic *ac* plane. (*c*) The frames of these tensors oscillate rapidly between two orientations that are related by the symmetry elements of $P2_1/n$. This point is discussed below, but it should be emphasized that regardless of the orientation

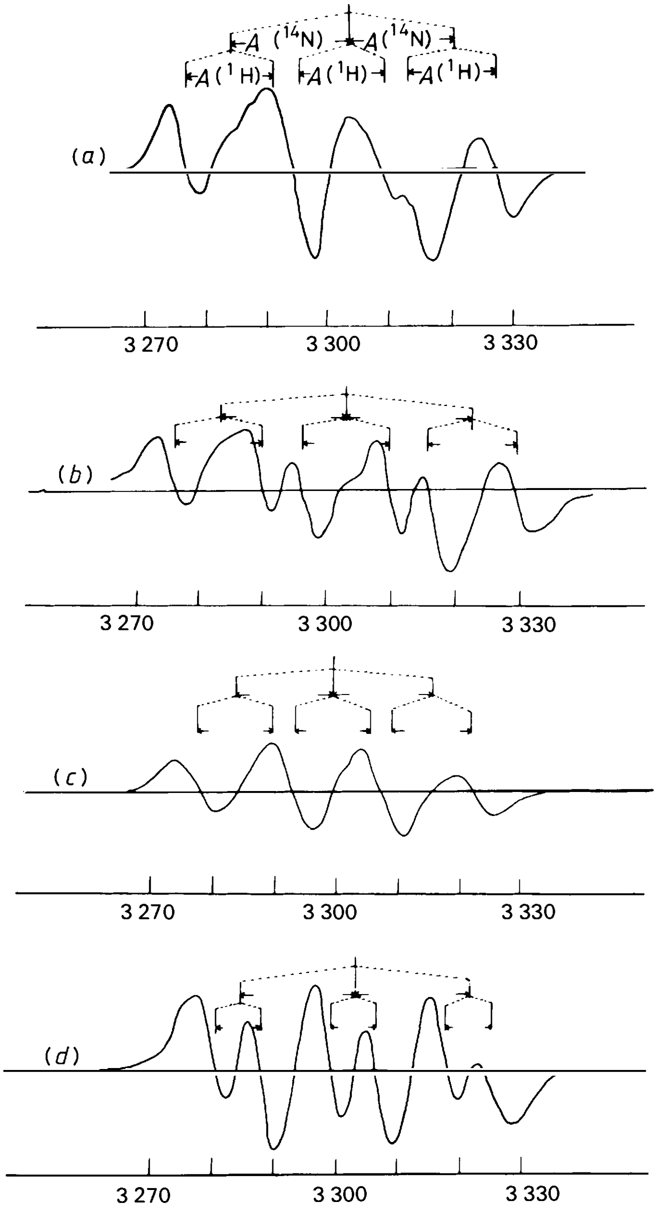


Figure 3. E.p.r. spectra of the radical (**7**) that is obtained by red-irradiation of a single crystal of the needle form of humulene nitrosite. The magnetic field is directed along the *x* axis in (*a*), along the *y* axis in (*b*), along the *z* axis in (*c*), and in the *xy* plane at 120° to the *x* axis in (*d*).

chosen for the direction of the applied magnetic field, six broad peaks were detected at most, in the e.p.r. spectra of the main radical obtained on brief red irradiation of this crystal, and spectral doubling in this case was never observed. The spectra are characteristic of a nitroxide radical in which one unpaired electron interacts with one ^{14}N nucleus and with one proton.

The spin-Hamiltonian of the main radical was assumed to have the form of equation (1), and g, $A(^{14}N)$, and $A(^{1}H)$ tensor

$$\mathscr{H} = \beta_e H\cdot g\cdot S + S\cdot A(^{14}N)\cdot I(^{14}N) + S\cdot A(^{1}H)\cdot I(^{1}H) \quad (1)$$

components for each orientation were obtained from interpretation of the e.p.r. spectra. The squares of these parameters were fitted to curves with the form of equation (2) by least-

$$W^2 = W_{xx}\cos^2\theta + 2W_{xy}\cos\theta\sin\theta + W_{yy}\sin^2\theta \quad (2)$$

squares analysis, where W is a measured g, or $A(^{14}N)$ or $A(^{1}H)$ component, and W_{xx}, W_{xy} and W_{yy}, and components of the squares of the g, or $A(^{14}N)$ or $A(^{1}H)$ tensors, thus obtained. The squares of the g, $A(^{14}N)$, and $A(^{1}H)$ tensors of the primary radical obtained by red irradiation of the needle form of humulene nitrosite, in the *xyz* frame of reference, are listed in Table 1, and when diagonalized, these data yield the principal values of the various tensors of the spin-Hamiltonian parameters and the corresponding direction cosines with respect to the *xyz* frame, (*i*), and monoclinic *abc* frame, (*ii*), that are listed in Table 2.

Table 1. Components of the squares of the g, $A(^{14}N)$, and $A(^{1}H)$ tensors, referred to the *xyz* frame, for the primary radical produced by red-irradiation of the needle form of humulene nitrosite.

$$g^2 \begin{pmatrix} 4.0182 & 0.000\,18 & -0.000\,58 \\ 0.000\,18 & 4.019\,65 & 0.001\,95 \\ -0.000\,58 & 0.001\,95 & 4.027\,63 \end{pmatrix}$$

$$[A(^{14}N)]^2 \begin{pmatrix} 333.3 & -139.7 & 182.8 \\ -139.7 & 363.7 & -180.2 \\ 182.8 & -180.2 & 230.1 \end{pmatrix} G^2$$

$$[A(^{1}H)]^2 \begin{pmatrix} 156.0 & 77.8 & -45.0 \\ 77.8 & 159.0 & 87.1 \\ -45.0 & 87.1 & 143.4 \end{pmatrix} G^2$$

The g, $A(^{14}N)$, and $A(^{1}H)$ tensors in Table 2 can be redefined in terms of their isotropic and anisotropic components, the latter making the direction cosines with the two co-ordinate frames that are listed in Table 2, to give the following results:

$$(g) = \begin{pmatrix} 2.0055 & 0 & 0 \\ 0 & 2.0055 & 0 \\ 0 & 0 & 2.0055 \end{pmatrix} + \begin{pmatrix} 0.0016 & 0 & 0 \\ 0 & -0.0007 & 0 \\ 0 & 0 & -0.0010 \end{pmatrix}$$

$$[A(^{14}N)] = \begin{pmatrix} 16.12 & 0 & 0 \\ 0 & 16.12 & 0 \\ 0 & 0 & 16.12 \end{pmatrix} + \begin{pmatrix} -7.68 & 0 & 0 \\ 0 & 9.31 & 0 \\ 0 & 0 & -1.62 \end{pmatrix} G$$

$$[A(^{1}H)] = \begin{pmatrix} -10.95 & 0 & 0 \\ 0 & -10.95 & 0 \\ 0 & 0 & -10.95 \end{pmatrix} + \begin{pmatrix} +7.6 & 0 & 0 \\ 0 & -2.65 & 0 \\ 0 & 0 & -4.95 \end{pmatrix} G$$

The isotropic contributions show[6] that the first radical that is formed on brief irradiation of the needle form of humulene nitrosite with red light is a monoalkyl nitroxide $H(R)N\overset{\cdot}{-}O$. The signs of the principal values of $[A(^{14}N)]$ are, therefore, all positive, and the signs of each of the corresponding principal values of $[A(^{1}H)]$ are all negative. These results, when combined with those obtained in our earlier polycrystalline studies,[3] show further that the mechanism of the early stages of red-photolysis of the needle form of humulene nitrosite is that outlined in the Scheme.

Irradiation of the nitroso group in (**1**) with red light causes an $\pi^* \longleftarrow n$ transition and the intermediate biradical (**5**) is formed. At this stage either: (*i*) hydrogen transfer takes place to give a monoalkylnitroxide biradical (**6**) which is then stabilized by loss of a hydrogen atom at C(6) to form the monoalkyl nitroxide

Table 2. Principal values and direction cosines of the g, $A(^{14}N)$, and $A(^{1}H)$ tensors, referred to the xyz frame (*i*) and monoclinic abc frame (*ii*) for the first radical produced by red-irradiation of a single crystal of the needle form of humulene nitrosite. The direction cosine matrices are in the forms (*i*) and (*ii*) where l_1, m_1, n_1 and l'_1, m'_1, n'_1 are the direction cosines of principal component 1 with respect to the xyz- and abc-frames, respectively.

$$\overset{(i)}{\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{pmatrix}} \quad \text{and} \quad \overset{(ii)}{\begin{pmatrix} l'_1 & l'_2 & l'_3 \\ m'_1 & m'_2 & m'_3 \\ n'_1 & n'_2 & n'_3 \end{pmatrix}}$$

$$g \begin{pmatrix} 2.0071 & 0 & 0 \\ 0 & 2.0048 & 0 \\ 0 & 0 & 2.0045 \end{pmatrix}$$

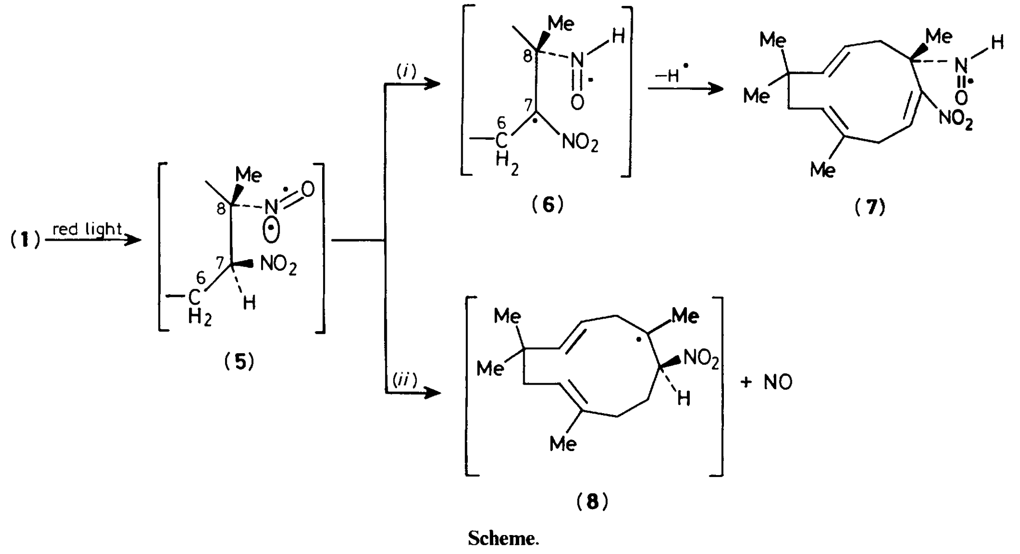
$$\overset{(i)}{\begin{pmatrix} -0.0506 & -0.2605 & -0.9641 \\ 0.2147 & -0.9455 & 0.2436 \\ 0.9715 & 0.1959 & -0.1045 \end{pmatrix}} \qquad \overset{(ii)}{\begin{pmatrix} -0.9751 & -0.1959 & -0.0924 \\ -0.2147 & 0.9455 & 0.2436 \\ 0.2419 & 0.2940 & -0.9245 \end{pmatrix}}$$

$$[A(^{14}\mathrm{N})] \begin{pmatrix} 8.44 & 0 & 0 \\ 0 & 25.43 & 0 \\ 0 & 0 & 14.5 \end{pmatrix} \mathrm{G}$$

$$\begin{pmatrix} -0.4203 & 0.5844 & -0.6958 \\ 0.3217 & -0.6214 & -0.7144 \\ 0.8485 & 0.5241 & -0.0738 \end{pmatrix} \qquad \begin{pmatrix} -0.8480 & -0.5239 & 0.732 \\ -0.3223 & 0.6211 & 0.7176 \\ 0.5793 & -0.4695 & 0.6678 \end{pmatrix}$$

$$[A(^{1}\mathrm{H})] \begin{pmatrix} -3.35 & 0 & 0 \\ 0 & -13.61 & 0 \\ 0 & 0 & -15.9 \end{pmatrix} \mathrm{G}$$

$$\begin{pmatrix} -0.5169 & 0.7416 & -0.4275 \\ 0.6201 & -0.0199 & -0.7843 \\ -0.5901 & -0.6705 & -0.4496 \end{pmatrix} \qquad \begin{pmatrix} 0.5906 & 0.6704 & 0.4493 \\ -0.6198 & 0.0244 & 0.7848 \\ 0.3904 & -0.8591 & 0.3305 \end{pmatrix}$$



Scheme.

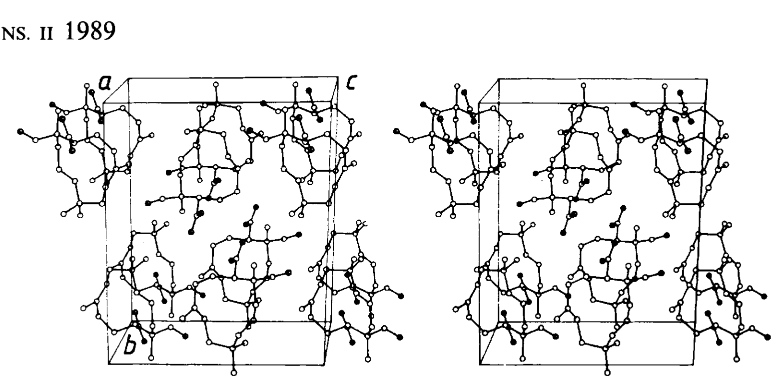


Figure 4. Stereoscopic view of the molecular packing within the unit cell of the needle form of humulene nitrosite.

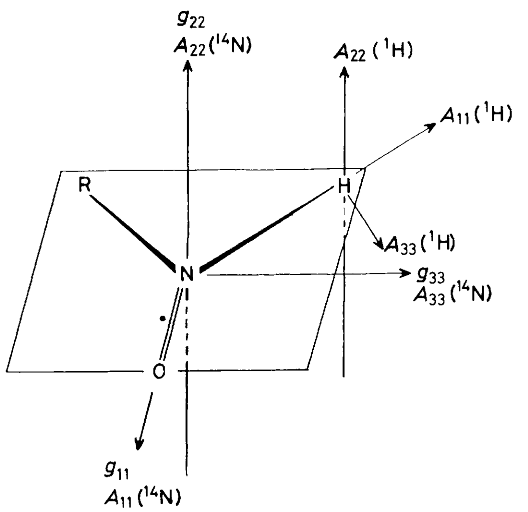


Figure 5. The principal directions of the g, $A(^{14}N)$, and $A(^{1}H)$ tensors orientated in the R–NH–O framework of a rigid monoalkyl nitroxide radical.

radical (**7**) observed in the single-crystal e.p.r. spectroscopic studies, or (*ii*) (**5**) undergoes homolysis of its C(8)–N bond to form the master radical (**8**) and nitric oxide (which have previously been shown[3] to be the source of other radicals and several diamagnetic products, that are detected in later stages of the photolysis). Formation of (**7**) rather than (**8**) strongly predominates in the early stages. Examination of the conformation of (**1**) in the needle form of solid humulene nitrosite (see Figure 4), shows that it is the C(7)H·NO_2 hydrogen atom that is transferred, and since we did not observe triplet state e.p.r. spectra in this work, the monoalkyl nitroxide radical must be (**7**).

In nitroxide radicals the largest g-tensor component is almost parallel to the direction of the N–O bond, and the largest component of the ^{14}N hyperfine-coupling tensor is known to be obtained when the magnetic field is almost parallel to the axis of the p_z orbital on the nitrogen atom.[6,8–10] The direction cosines listed in Table 2, therefore, enable the mean plane through the σ-frame of the H(R)N≐O fragment to be located within the monoclinic unit cell. They show that the N–O bond makes an angle of about 12° to the a axis of the unit cell and that the normal to the mean plane through the σ-frame of the radical makes an angle of about 50° with the unit cell b axis. Furthermore, in the crystal structure of the parent humulene nitrosite C(5), C(6), C(7), and C(8) are almost coplanar so that in the reaction (**1**) $\xrightarrow{h\nu}$ (**7**) only minor changes in the coordinates of these four atoms are needed. The NO_2 group does need to move so that its nitrogen atom moves into this plane, but there is more than enough space in the crystal structure to easily accommodate this. The e.p.r. spectroscopic results also show that the orientation of the N–O bond in the radical (**7**) does not coincide with the corresponding orientation in the parent humulene nitrosite molecule (**1**). The translational energy of the C(7)-H hydrogen atom transferred in the reaction (**1**) $\longrightarrow$ (**7**) appears to be converted into a rotational motion that causes the –HN≐O residue to rotate through almost 180°, thereby the N–O bond becomes aligned almost parallel to the a axis of the unit cell.

The spin-Hamiltonian parameters expected for a rigid monoalkyl nitroxide radical are,[6,8–10] approximately,

$$(g) = \begin{pmatrix} 2.0063 & 0 & 0 \\ 0 & 2.0063 & 0 \\ 0 & 0 & 2.0063 \end{pmatrix} + \begin{pmatrix} 0.0029 & 0 & 0 \\ 0 & -0.0030 & 0 \\ 0 & 0 & 0.0001 \end{pmatrix}$$

$$[A(^{14}N)] = \begin{pmatrix} 14.7 & 0 & 0 \\ 0 & 14.7 & 0 \\ 0 & 0 & 14.7 \end{pmatrix} + \begin{pmatrix} -4.3 & 0 & 0 \\ 0 & 13.9 & 0 \\ 0 & 0 & -9.6 \end{pmatrix} \mathrm{G}$$

$$[A(^{1}H)] = \begin{pmatrix} -11.1 & 0 & 0 \\ 0 & -11.1 & 0 \\ 0. & 0. & -11.1 \end{pmatrix} + \begin{pmatrix} 10.3 & 0 & 0 \\ 0 & -1.2 & 0 \\ 0 & 0 & -9.1 \end{pmatrix} \mathrm{G}$$

and approximate orientations for the principal directions of these tensors in the R–NH–O frame of the radical are shown in Figure 5. The amplitudes of the anisotropic contributions to g, $[A(^{14}N)]$, and $[A(^{1}H)]$ of radical (**7**) are all less than those expected for a rigid system, and they show that the radical exhibits considerable thermal motion within the solid. The e.p.r. spectroscopic results for (**7**) can be qualitatively explained if an anisotropic libration, about an axis that is nearly parallel to the direction of the N–O bond, is superimposed on an isotropic thermal movement of the R–NH–O framework. Examination of the crystal structure of (**1**) indicates that this anisotropic contribution could arise from libration of the whole molecular frame of (**7**) about the normal to the mean plane through the cycloundecatriene ring, and to account for the e.p.r. spectroscopic results its frequency must be high enough almost to remove the expected differences in g_{22} and g_{33}, but not high enough to remove the differences in $A_{22}(^{14}N)$ and $A_{33}(^{14}N)$, *i.e.* this librational frequency must lie within the range $14 \leqslant \nu_{\text{libration}} \leqslant 60$ MHz. Although the centrosymmetrically related pairs of molecules in $P2_1/n$ are crystallographically distinguishable, the orientation of the R–NH–O framework in the unit cell of the needle form of humulene nitrosite (when combined with thermal vibration within the solid) coincidentally causes the effective principal directions of the tensors in the spin-Hamiltonian for each of the four molecules in the unit cell to be almost parallel. As a result, the crystallographically distinguishable molecules in this solid can not be distinguished by e.p.r. methods at 290 K.

More precise information about molecular motions within this solid would require its spin-Hamiltonian parameters to be investigated over a wide range of steadily decreasing temperatures, so that the librational motions are frozen out and the expected e.p.r. spectral doubling could then be observed.

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References

1 A. C. Chapman, *J. Chem. Soc.*, 1895, **67**, 54.
2 A. C. Chapman, *J. Chem. Soc.*, 1895, **67**, 780.
3 D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2533.
4 D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1385.
5 Z. F. Khan, D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1259.
6 A. A. Freer, D. K. MacAlpine, J. A. Peacock, and A. L. Porte, *J. Chem. Soc., Perkin Trans. 2*, 1985, 971.
7 D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc., Perkin Trans. 1*, 1981, 999.
8 O. H. Griffith, D. W. Cornell, and H. M. McConnell, *J. Chem. Phys.*, 1965, **43**, 2909.
9 O. H. Griffith and A. S. Waggoner, *Acc. Chem. Res.*, 1969, **2**, 17.
10 O. Kikuchi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1187.

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