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

Zia F. Khan, Andrew L. Porte,* and Janette E. Schubert
Department of Chemistry, The University of Glasgow, Glasgow G12 8QQ

E.p.r. studies of the first radical that is produced when a single crystal of the platelet form of humulene nitrosite is irradiated with red light enable the tensor components of its spin-Hamiltonian to be evaluated, and the principal directions of its *g*, $A(^{14}N)$, and $A(^{1}H)$ tensors to be orientated with respect to the crystallographic axes of the monoclinic unit cell. The radical is a monoalkyl nitroxide to which the structure (**2**) is assigned: it is a geometric isomer of the corresponding cycloundecatriene derivative that is obtained when the needle form of humulene nitrosite is red-irradiated. Superimposition of relatively minor librational motions in the solid, causes the principal directions within its different nitroxides to become effectively parallel, so that the two crystallographically distinguishable molecules of (**2**) in the unit cell can not be distinguished by e.p.r. methods at 293 K.

The molecular conformations in the platelet form of humulene nitrosite, Figure 1, and in the corresponding needle form of this substance, Figure 1 of the preceding paper, are the two lowest energy forms of the four conformational isomers that might, in principle, be obtained by rotating the alkenic segments of this molecule through the cycloundecadiene ring.[1–3] The crystal habits and the crystal structures of the two solids also differ, and we therefore wondered if single-crystal e.p.r. studies would reveal any differences in the red photochemical reactions within the two crystalline forms. The results obtained when a single crystal of the needle form of humulene nitrosite is irradiated for a short time with red light are described in the preceding paper.[4] Corresponding e.p.r. studies carried out on a platelet crystal are described below.

Results and Discussion

Blue platelet crystals were obtained by slowly recrystallizing humulene nitrosite, in darkness, from a dilute ethanolic solution over a period of *ca.* fifteen days, a procedure[5] that yields a mixture of large platelets and some small needles, from which the platelets are easily separated manually.

The right-handed orthogonal framework *xyz* shown in Figure 2(*b*) was identified in a well-formed platelet. The crystal was mounted inside a standard TE_{102} rectangular cavity of a Decca e.p.r. spectrometer, irradiated with red light; e.p.r. spectra were then recorded as described in the preceding paper.[4] Some of the single-crystal spectra obtained in this way are shown in Figure 3.

The platelet form of humulene nitrosite belongs to the monoclinic system, $a = 7.873(6)$, $b = 16.660(9)$, $c = 12.140(6)$ Å, $\beta = 101.94(5)°$, $Z = 4$, space group $P2_1/c$,[3] and morphological examination of the crystal shows that the monoclinic *a*, *b*, and *c* axes are orientated as shown in Figure 2(*b*). The Miller indices of the prominent faces of the platelet crystal are shown in Figure 2(*a*) and straightforward geometrical arguments lead to the following values for the direction cosines of *a*, *b*, and *c* with respect to the *x*, *y*, and *z* axes.

Axis	D cos w.r.t. *x*, *y*, and *z*
a	0, 0, and −0.9962
b	0.5878, 0.8090, and 0
c	0.8090, −0.5878, and 0.2062

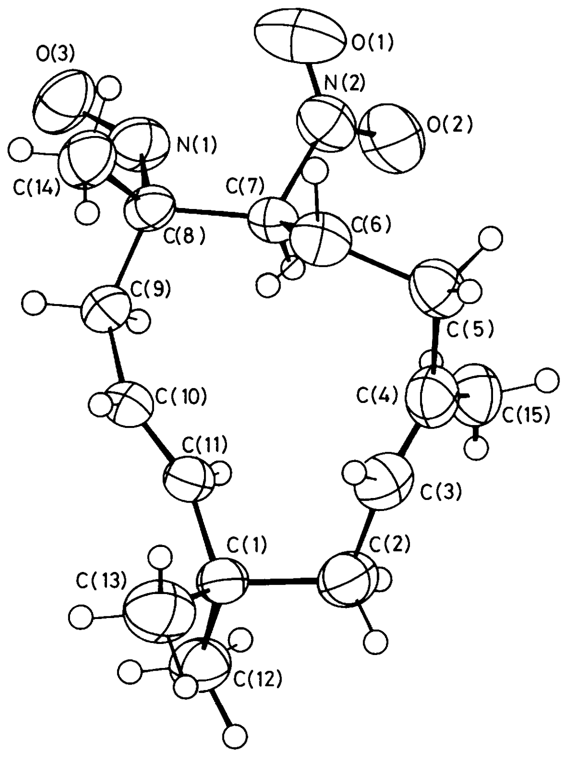


Figure 1. The molecular conformation in the platelet form of humulene nitrosite.

The axis of the spiral defect that commonly appears in these crystals is the normal to the (011) plane, which *X*-ray analysis has already shown to be one of the planes in which the molecules of humulene nitrosite preferentially pack within this solid.[3]

The four molecules in the unit cell of $P2_1/c$ form two centrosymmetric pairs that are related through the *ac* glide

---

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

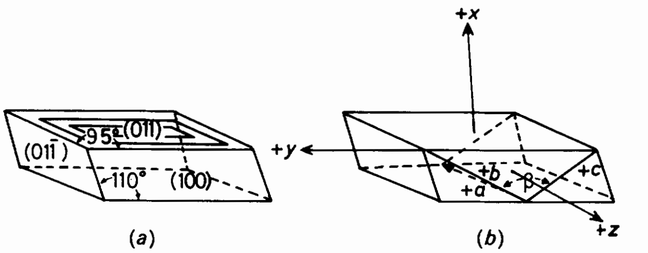


Figure 2. The habit of the platelet used in the e.p.r. analysis, showing (*i*) the spiral defect and the Miller indices of the prominent faces and (*ii*) the orientations of the orthogonal, *xyz*, and monoclinic, *abc*, frames in the crystal.

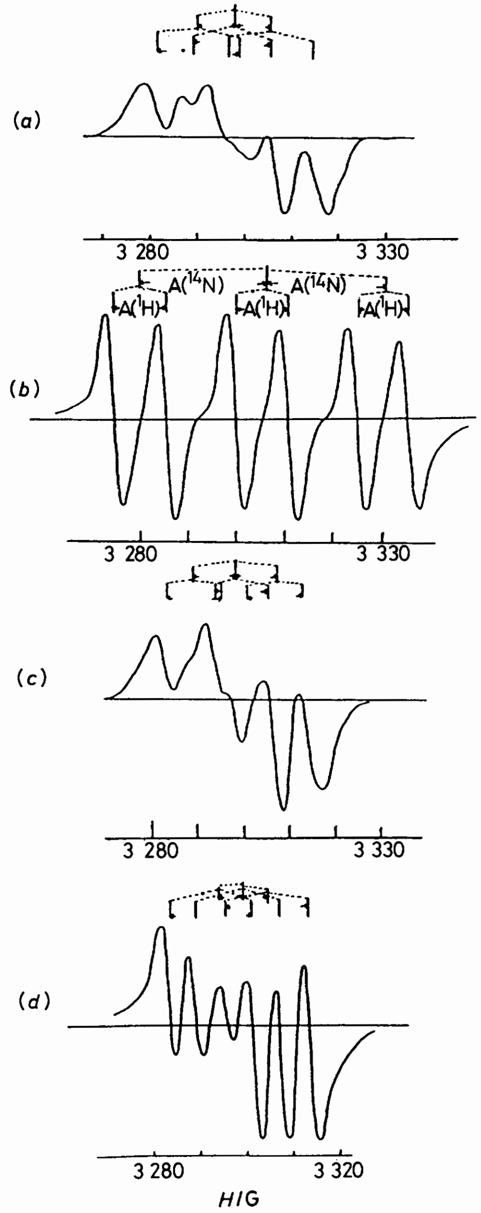
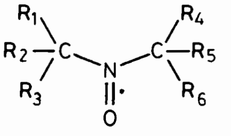


Figure 3. E.p.r. spectra of the radical (7) that is obtained by red-irradiation of a single crystal of the platelet form of humulene nitrosite. The magnetic field is directed along the *x* axis in (*a*), along the *y* axis in (*b*), along the *z* axis in (*c*), and in the *zx* plane at 120° to the $+x$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

plane of the cell, and so two superimposed sets of equally intense e.p.r. spectra are expected for each chemically distinguishable radical that is formed in the irradiation, unless the magnetic field is applied parallel to the monoclinic *b* axis, or unless it lies in the *ac* plane, when the symmetry properties of the space group then require the two spectra to be superimposed. E.p.r. spectra in this crystal do, in fact, contain two overlapping sets of signals, but the second of these is consistently very much less intense than the first, and it is obvious from the spectra that these two sets of signals are not related. The weak component in the spectra arises from a ditertiary alkyl nitroxide radical (**1**).



(1)

The strong component in the signals never contains more than six absorption peaks, and spectral doubling has never been observed in this work. The strong component of the spectra arises from a nitroxide radical in which one unpaired electron interacts with one ^{14}N nucleus and one proton, and standard procedures[6] applied to its single-crystal e.p.r. spectra lead to the squares of the g, $A(^{14}N)$, and $A(^{1}H)$ tensors listed in Table 1, for this primary radical obtained by red-irradiation of the platelet form of humulene nitrosite. When diagonalized and transformed by means of the direction cosines listed above, the data in Table 1 yield the principal values of the various tensors and the corresponding direction cosines with respect to the *xyz* frame, (*i*), and the monoclinic *abc* frame, (*ii*), that are listed in Table 2. Redefining of the g, $A(^{14}N)$ and $A(^{1}H)$ tensors in Table 2 in terms of their isotropic and anisotropic components, the latter making the direction cosines with the two frames that are listed in the table, gives the results listed in Table 3.

The isotropic contributions are very close to those already found in similar work on caryophyllene nitrosite[6] and on the needle form of humulene nitrosite,[4] and they show that the more abundant of the two radicals that are first obtained when the platelet form of humulene nitrosite is irradiated with red light is also a monoalkyl nitroxide $H(R)N\dot{-}O$.

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 platelet form of humulene nitrosite.

$$g^2 \quad \begin{pmatrix} 4.0314 & 0.0002 & 0.0000 \\ 0.0002 & 4.0136 & -0.0026 \\ 0.0000 & -0.0026 & 4.0825 \end{pmatrix}$$

$$[A(^{14}N)]^2 \quad \begin{pmatrix} 54.4 & 1.0 & 39.2 \\ 1.0 & 619.1 & 33.1 \\ 39.2 & 33.1 & 82.5 \end{pmatrix} \quad G^2$$

$$[A(^{1}H)]^2 \quad \begin{pmatrix} 237.8 & 41.9 & -137.8 \\ 41.9 & 112.9 & -45.2 \\ -137.8 & -45.2 & 132.4 \end{pmatrix} \quad G^2$$

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 the monoclinic abc frame (*ii*) for the first radical produced by red irradiation of a single crystal of the platelet form of humulene nitrosite. The direction cosine matrices are in the forms

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

where l_1, m_1, n_1 and l'_1, m'_1, n'_1 are the d cos of the principal component 1 with respect to the xyz and abc frames, respectively.

$$g \begin{pmatrix} 2.0078 & 0 & 0 \\ 0 & 2.0033 & 0 \\ 0 & 0 & 2.0072 \end{pmatrix}$$

$$\overset{(i)}{\begin{pmatrix} 0.9998 & 0.0129 & 0.0148 \\ 0.0152 & -0.9862 & -0.1650 \\ 0.0124 & -0.1652 & 0.9862 \end{pmatrix}} \qquad \overset{(ii)}{\begin{pmatrix} -0.0124 & 0.0165 & -0.9824 \\ 0.6000 & -0.7903 & -0.1248 \\ 0.8031 & 0.5561 & 0.2034 \end{pmatrix}}$$

$$[A(^{14}N)] \begin{pmatrix} 4.9 & 0 & 0 \\ 0 & 24.9 & 0 \\ 0 & 0 & 10.4 \end{pmatrix} \text{G}$$

$$\overset{(i)}{\begin{pmatrix} -0.8225 & -0.0060 & -0.5687 \\ -0.0302 & -0.9981 & 0.0543 \\ 0.5679 & -0.0618 & -0.8208 \end{pmatrix}} \qquad \overset{(ii}{\begin{pmatrix} -0.5657 & 0.0616 & 0.8177 \\ -0.5079 & -0.8110 & -0.2904 \\ -0.5306 & 0.5691 & -0.6613 \end{pmatrix}}$$

$$[A(^{1}H)] \begin{pmatrix} -18.7 & 0 & 0 \\ 0 & -10.0 & 0 \\ 0 & 0 & -5.9 \end{pmatrix} \text{G}$$

$$\overset{(i)}{\begin{pmatrix} -0.7918 & 0.3178 & -0.5216 \\ -0.2484 & -0.9477 & -0.2003 \\ 0.5580 & 0.0291 & -0.8293 \end{pmatrix}} \qquad \overset{(ii)}{\begin{pmatrix} -0.5559 & -0.0290 & 0.8261 \\ -0.6664 & -0.5799 & -0.4686 \\ -0.3795 & 0.8202 & -0.4752 \end{pmatrix}}$$

Table 3.

$$g = \begin{pmatrix} 2.0061 & 0 & 0 \\ 0 & 2.0061 & 0 \\ 0 & 0 & 2.0061 \end{pmatrix} + \begin{pmatrix} 0.0017 & 0 & 0 \\ 0 & -0.0028 & 0 \\ 0 & 0 & 0.0011 \end{pmatrix}$$

$$A(^{14}N) = \begin{pmatrix} 13.4 & 0 & 0 \\ 0 & 13.4 & 0 \\ 0 & 0 & 13.4 \end{pmatrix} + \begin{pmatrix} -8.5 & 0 & 0 \\ 0 & 11.5 & 0 \\ 0 & 0 & -3.0 \end{pmatrix} \text{G}$$

$$A(^{1}H) = \begin{pmatrix} -11.5 & 0 & 0 \\ 0 & -11.5 & 0 \\ 0 & 0 & -11.5 \end{pmatrix} + \begin{pmatrix} -7.2 & 0 & 0 \\ 0 & 1.5 & 0 \\ 0 & 0 & 5.6 \end{pmatrix} \text{G}$$

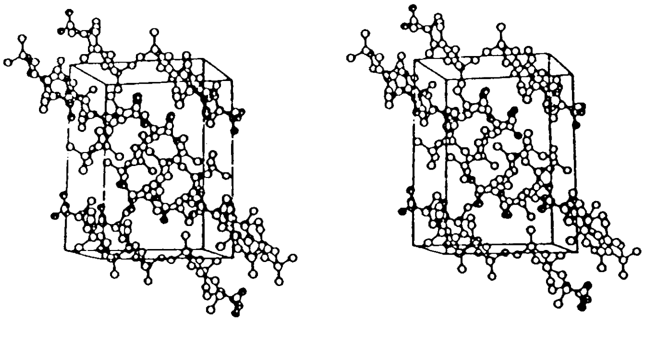
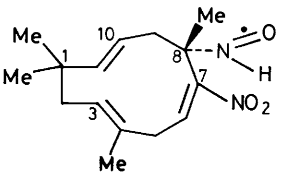


Figure 4. Stereoscopic view of the molecular packing within the unit cell of the platelet form of humulene nitrosite.



(2)

The near coincidence of the directions of the smallest principal value of g, the largest principal value of $A(^{14}N)$, and the intermediate principal value of $A(^{1}H)$, *i.e.* g_{22}, A_{22} (^{14}N) and $A_{22}(^{1}H)$, respectively, in Table 2, is expected on theoretical grounds,[6–9] and enables the direction within the unit cell of the axis of the p_z orbital on the nitroxide nitrogen atom to be identified. The p_z orbital lies almost at right angles to the mean plane through the 11-membered ring. Furthermore, when this observation is combined with the direction cosines of the intermediate, 10.37 G, component of $A(^{14}N)$, it follows that the orientation of the C(8)–(HN)$\dot{=}$O residue of the radical almost coincides with the original orientation of the C(8)–N=O fragment of the host nitrosite. The conformation and orientation of the parent molecule, shown in Figure 4, the proximity of the C(7)–H hydrogen atom to the original lone pair of electrons in the nitroso group, the structure and orientation of the radical in the host humulene nitrosite unit cell, and the results obtained from our earlier polycrystalline studies,[1] all imply that the mechanisms of the early stages of red photolysis of the platelet form of humulene nitrosite almost exactly parallel the corresponding reactions encountered in the needle form.[4]

Red-irradiation of the platelet form causes a nitroso $\pi^* \longleftarrow n$ transition to take place, and two competing parallel reactions of the kind described in the preceding paper[4] then follow. Similar competing reactions have also been identified in the red photolysis of caryophyllene nitrosite,[6] and they seem to be common to compounds of this type. Biradicals or triplet species have never been observed during our studies of the photolysis reactions of the nitrosites so the cycloundecatriene structure (**2**), or possibly an isomer formed by an allylic shift in (**2**), is therefore assigned to the monoalkyl nitroxide observed in this work. Compound (**2**) and the monoalkyl nitroxide radical (**7**) that is obtained[4] when the needle form of humulene nitrosite is red-irradiated are geometric isomers, each isomer being obtained from the other by rotating the two alkene segments $>$C(3)=C(4)$<$ and $>$C(10)=C(11)$<$ through the cycloundecatriene ring by 180°.

The anisotropic contributions to the principal components of g_{22} and $A_{22}(^{14}N)$ are only slightly smaller than the corresponding values observed for the similar monoalkyl nitroxide radical that is obtained from caryophyllene nitrosite,[6] but the other anisotropic components of g, $A(^{14}N)$, and $A(^{1}H)$ are noticeably less in the case of (**2**). These values can be understood by considering the stereoscopic view of the crystal structure (Figure 4) and if the radical (**2**) simultaneously undergoes librational motion about the normal to its mean plane whilst the C(8)–(NH)$\dot{=}$O residue also flips rapidly back and forth, about the C(8)–N bond, between the orientations of the two nitroso residues that are related by the glide plane in the host humulene nitrosite crystal structure. Only small amplitudes of libration are needed to cause the effective principal directions of the two sets of magnetic-interaction tensors in this crystal to become almost parallel. Relatively minor librations of this kind would also explain why the e.p.r. spectra of the two crystallographically distinguishable nitroxide radicals (**2**) in the host humulene nitrosite crystal structure are superimposed. As was the case in the red-irradiated needle form,[4] although the orientations of the two crystallographically distinguishable molecules of (**2**) in the space group $P2_1/c$ are quite different, by chance their C(8)–(NH)$\dot{=}$O residues are effectively parallel at 293 K, and single crystal e.p.r. methods cannot, therefore, discriminate between them.

Acknowledgements

We thank the Ministry of Education of the Government of Pakistan for a Central Overseas Training Scholarship to (Z. F. K.), the SERC for magnetic resonance facilities, Professor G. A. Sim for carrying out the *X*-ray work, and Mr. A. Evans for technical assistance.

References

1 D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2533.
2 D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1385.
3 Z. F. Khan, D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc. Perkin Trans. 2*, 1983, 1259.
4 Z. F. Khan and A. L. Porte, *J. Chem. Soc., Perkin Trans. 2*, 1989, preceding paper.
5 D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc., Perkin Trans. 1*, 1981, 999.
6 A. A. Freer, D. K. MacAlpine, J. A. Peacock, and A. L. Porte, *J. Chem. Soc., Perkin Trans. 2*, 1985, 971.
7 O. H. Griffith, D. W. Cornell, and H. M. McConnell, *J. Chem. Phys.*, 1965, **43**, 2909.
8 O. H. Griffith and A. S. Waggoner, *Acc. Chem. Res.*, 1969, **2**, 17.
9 O. Kikuchi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1187.

Received 4*th January* 1989; *Paper* 9/00052F