

Conclusion

The geometry of *trans*-diphenyl(2-phenyl-3-chromanyl)methanol (II) appears to be the more diaxial for a vicinally disubstituted six-membered ring, in the absence of polar effects. Comparison with the molecular structure of *trans*-dimethyl 2,2'-(1,2-cyclohexylene)bis(2-methylpropanoate) (I) previously reported shows that in our compound the dihedral angle between the substituents is close to the value of 173° found in cyclohexane for vicinal axial C—H bonds [162 (0.5)° in II instead of 134.5 (0.5)° in I]. Furthermore, the flattening in the substituted part of the ring [endocyclic torsion angle of 55 (0.5)°] is far less pronounced than in I [37.4 (5)°] and very close to that of cyclohexane itself (56°).

This X-ray structure determination shows also that the chroman ring of the *cis* isomer adopts a C(3) sofa conformation bearing the 2-phenyl substituent in axial position and the bulkier 3-substituent in an equatorial one. These two substituents are brought closer by a rather strong hydrogen bond of the OH... π type which contributes to the rigidity of the whole molecule.

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An X-ray Crystallographic Study on the Geometry of the C— \bar{N} —O Group and the [1,5] Sigmatropic Rearrangement from C-Nitroso Compounds to Oximes

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Abstract

Single-crystal X-ray analyses of *N*-(4-chlorophenyl)-3-methylamino-2-nitroso-2-butenamide (I) and 5,5-dimethyl-2-nitroso-3-phenylamino-2-cyclohexen-1-one (II) show that in both compounds the —N=O groups are implied in conjugated double-bond systems and their geometries are intermediate between those of oximes and C-nitroso derivatives and very close to

those observed in isonitroso >C=N-O^- ions. The comparison of bond distances and angles of the C— \bar{N} —O group with those of several C-nitroso compounds and oximes allows the extrapolation of the geometry of the transition state of an asymmetric [1,5] sigmatropic rearrangement describing the interconversion from nitrosovinylamine to iminoxime. The present conclusions are compared with the results of theoretical *ab initio* calculations obtained by other

authors on a strictly similar system. Details on crystal structure determinations are as follows: I: $C_{11}H_{12}ClN_3O_2$, $M_r = 253.7$, space group $Pbca$ with $a = 18.376$ (4), $b = 11.762$ (3), $c = 10.982$ (3) Å, $Z = 8$, $D_x = 1.42$ Mg m $^{-3}$, $\mu(Cu K\alpha) = 2.69$ mm $^{-1}$. II: $C_{14}H_{16}N_2O_2$, $M_r = 244.3$, space group $C2/c$ with $a = 13.040$ (3), $b = 10.178$ (3), $c = 19.239$ (4) Å, $\beta = 92.33$ (3) $^\circ$, $Z = 8$, $D_x = 1.27$ Mg m $^{-3}$, $\mu(Cu K\alpha) = 0.62$ mm $^{-1}$. Both structures were refined from diffractometer data and final R values were 0.053 (1588 observed reflections) and 0.035 (1144 observed reflections) for I and II, respectively.

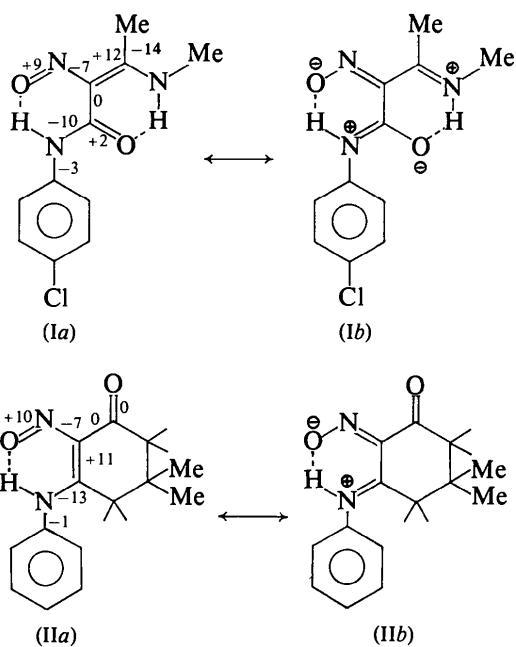
Introduction

C-nitroso compounds are known to exist as blue or blue-green coloured monomers when fused or dissolved in solution. However, they tend to give colourless azodioxide dimers in the solid state, which can exist in *cis* and *trans* forms. Accordingly, coloured monomeric C-nitroso compounds are unusual in crystals and are observed only when the dimer formation is hindered either by the packing arrangement or by the formation of inter- or intramolecular hydrogen bonds involving the N—O group. During an investigation on vicinal multifunctional compounds we have reported that α -hydroximino- β -imino-ketones or amides exist in solution in equilibrium with their tautomeric α -nitroso- β -enamino forms (Veronese, Scrimin, Bergamini & Gambaro, 1982; Veronese, Cavicchioni, Scrimin, Vecchiati & Bertolasi, 1982). Crystals of colourless hydroximino-imino and/or coloured nitroso-enamino tautomers can be isolated. We have already reported the crystal structure determination of colourless *E,Z*-4-(*p*-tolylimino)-2,3-pentanedione 3-oxime (Bertolasi, Gilli & Veronese, 1982) and in the present paper we report the crystal structures of two coloured nitroso-enamino derivatives. It will be shown that the comparison of C—N and N—O bond distances and C—N—O angles of the present compounds with those observed in C-nitroso compounds and oximes allows the determination of the probable geometry of the transition state of the title rearrangement.

The geometry of the C—N—O group

The ORTEP (Johnson, 1971) views of molecules I and II are shown in Figs. 1 and 2. Interatomic distances, angles and a selection of torsion angles are given as part of the Appendix.

Molecule I is built up of three rings, the phenyl *A* [atoms C(1)—C(6); $\chi^2 = 26.4$] and two other rings closed by intramolecular hydrogen bonds, that is *B* [atoms N(1), C(7), C(8), N(2), O(2); $\chi^2 = 87.5$] and *C* [atoms O(1), C(7), C(8), C(9), N(3); $\chi^2 = 291.9$],



forming the interplanar angles $A-B = 11.5$ (1) and $B-C = 3.7$ (1) $^\circ$. As for bond distances, scheme *Ia* reports the limit formula in the absence of any conjugation together with the differences (pm) between the actual and pure single or double bond (Table 1) lengths. The pattern of the differences is consistent with a relevant contribution of the polar form *Ib*, which consists of two *zig-zag* planar systems of conjugation running horizontally, not coupled through the C(7)—C(8) bond and mutually stabilized in their polar forms by the hydrogen bonds N(1)⋯O(2) [2.579 (3) Å] and N(3)⋯O(1) [2.626 (3) Å].

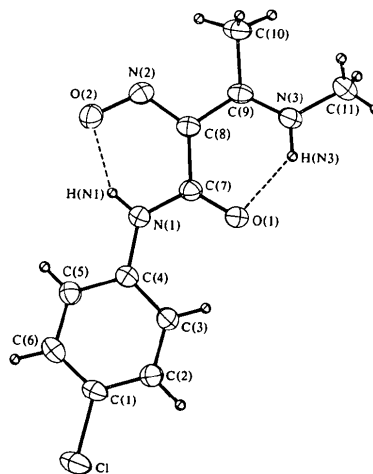


Fig. 1. A view of molecule I, showing the thermal ellipsoids at 40% probability (Johnson, 1971).

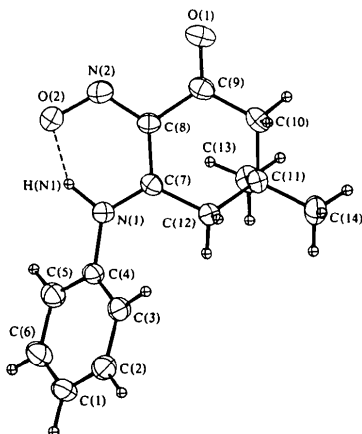


Fig. 2. A view of molecule II, showing the thermal ellipsoids at 40% probability (Johnson, 1971).

Table 1. Assumed equilibrium bond distances (Å) for some relevant couples of atoms

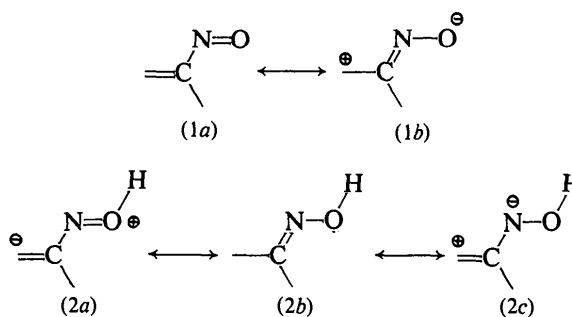
Values are mostly taken from Dunitz (1979).

C(sp ³)-C(sp ³)	1.54	C(sp ²)-N(sp ³)	1.44
C(sp ³)-C(sp ²)	1.51	C(sp ²)-N(sp ²)	1.41
C(sp ²)-C(sp ²)	1.48	C(sp ²)=O	1.22
C(sp ²)=C(sp ²)	1.33	N(sp ²)=O	1.20

In molecule II the phenyl ring *A* [atoms C(1)-C(6); $\chi^2 = 9.2$] makes an angle of 49.7 (1)° with the mean plane through the ring *B* [atoms N(1), C(7), C(8), N(2), O(2); $\chi^2 = 199.6$], while the third ring *C* [atoms C(7)-C(12); $\chi^2 = 326.0$] adopts a half-chair conformation with C(11) as bow atom. Ring *B* is closed by the hydrogen bond N(1)···O(2) = 2.483 (2) Å. By subtracting from the actual bond distances those of Table 1, the figures reported in IIa (pm) are obtained, which show the relevant contribution of the polar form IIb to the ground state of the molecule.

In both molecules the bond situation, as far as the N=O group is concerned, is intermediate between that of a C-nitroso compound and of an isonitroso $>C=N-O^-$ ion; comparison with the crystal structures of two of these ions (Raston & White, 1976) indicates it is much closer to the latter. The reason has to be sought in the stabilization of the polar forms Ib and IIb by intramolecular hydrogen bonds. These are unusually strong, as can be seen by comparing the observed N···O distances with the value of 2.89 (14) Å obtained as an average on 883 homonuclear crystals by Kuleshova & Zorkii (1981). Moreover, comparison of I and II shows that the N(1)···O(2) distance is significantly shorter in II, which can be accounted for by the synergic mechanism in the setting up of the opposite charges allowed in the cyclic conjugated structure of II. From another point of view, the

presence of the intramolecular hydrogen bond makes these molecules, in some way, intermediate between C-nitroso compounds and oximes. This suggests the idea that the C-N-O geometry could change in a continuous way from C-nitroso compounds to oximes passing through isonitroso ions. The compounds to be chosen for such an analysis are those where changes in C-N and N-O distances are intercorrelated. A glance at the possible canonical forms for these compounds (1a,b; 2a,b,c) shows that the only compounds to be excluded are the oximes with electron-withdrawing groups, as they lead to longer C-N without any change of the N-O bonds (2c).



In Table 2 the compounds chosen are reported. They include all C-nitroso compounds available in the literature and a selection of oximes suiting the above criterion.

Fig. 3(a) reports a plot of the N-O vs C-N bond lengths for the compounds of Table 2. The points are arranged on a symmetrical smooth curve. Talberg

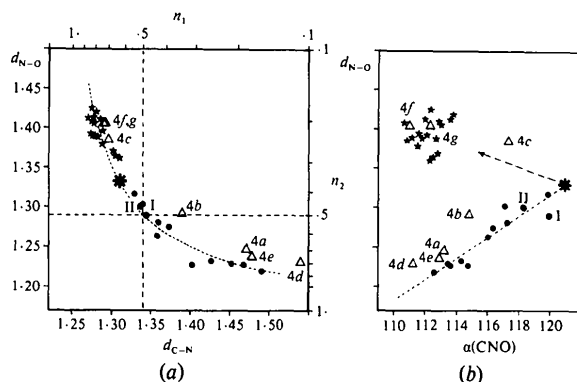


Fig. 3. (a) A plot of N-O vs C-N bond distances (Å) for C-nitroso compounds (full circles) and oximes (stars). [The dotted line has been calculated by means of equation (1) (see text).] (b) A plot of N-O bond distances (Å) vs C-N-O bond angles (°) for the same compounds. (The dotted line is the linear regression curve calculated from C-nitroso compounds only.) (a), (b) Open triangles refer to the optimized *ab initio* values obtained by Bouma & Radom (1979) for the nitrosovinyl alcohol-glyoxal monoxime system described in the text and the asterisks mark the hypothetical geometry of the transition state 3b (see text).

Table 2. Geometrical parameters for the C—N—O group in C-nitroso compounds and oximes

X = X-ray diffraction; MW = microwave; rt = room temperature.

	Method	Bond distances (Å)		Bond angles	References
		C—N	N—O	(°) C—N—O	
Nitrosomethane	MW	1.49 (3)	1.22 (3)	112.6 (10)	(a)
<i>p</i> -Nitrosoanisole	<i>X</i> 118 K	1.467 (10)	1.228 (8)	113.6 (6)	(b)
Ethyl <i>m</i> -nitroso- <i>trans</i> -cinnamate	<i>X</i> 108 K	1.451 (4)	1.229 (3)	113.5 (3)	(c)
5-Nitrososalicylic acid	<i>X</i> 108 K	1.426 (2)	1.234 (2)	114.3 (2)	(d)
Nitrosyl cyanide	MW	1.401 (5)	1.228 (5)	114.7 (10)	(e)
4-Nitroso-5-triphenylphosphoranylideneaminobenzo[1,2- <i>c</i> :3,4- <i>c'</i>]difurazan	<i>X</i> rt	1.358 (9)	1.265 (8)	116 (1)	(f)
<i>N,N,N',N'</i> -Tetramethyl-1,5-diamino-4-nitrosobenzene	<i>X</i> 173 K	1.372 (2)	1.276 (2)	116.3 (2)	(g)
Magnesium <i>p</i> -nitrosophenolate hexahydrate	<i>X</i> 108 K	1.359 (1)	1.282 (1)	117.2 (1)	(h)
Sodium <i>p</i> -nitrosophenolate trihydrate	<i>X</i> 111 K	1.340 (1)	1.303 (1)	117.1 (1)	(i)
Barium <i>N,N'</i> -dimethyl-isonitrosomalonamide	<i>X</i> rt	1.328 (6)	1.318 (5)	119.8 (5)	(j)
Compound I	<i>X</i> rt	{ 1.344 (3)	1.290 (3)	119.9 (2)	(k)
Compound II		{ 1.337 (2)	1.301 (2)	118.3 (1)	
<i>p</i> -Benzoquinone oxime	<i>X</i> rt	{ 1.302 (3)	1.371 (3)	112.8 (2)	(l)
		{ 1.310 (3)	1.362 (3)	112.3 (2)	
α -5-(2-Chloroethoxy)- <i>o</i> -benzoquinone 2-oxime	<i>X</i> 93 K	1.306 (7)	1.365 (6)	112.5 (6)	(m)
Obidoxime chloride	<i>X</i> rt	1.288 (3)	1.379 (3)	111.5 (2)	(n)
<i>E,E</i> -3-(<i>p</i> -Tolylimino)-2-butanone oxime	<i>X</i> rt	{ 1.278 (2)	1.390 (2)	112.7 (2)	(o)
		{ 1.282 (3)	1.389 (2)	111.8 (2)	
<i>E,Z</i> -4-(<i>p</i> -Tolylimino)-2,3-pentanedione 3-oxime	<i>X</i> rt	1.288 (4)	1.386 (4)	110.8 (3)	
<i>syn</i> -4-Pyridenecarboxaldehyde oxime	<i>X</i> rt	1.275 (8)	1.390 (7)	111.1 (5)	(p)
<i>syn</i> -4-Pyrimidencarboxaldehyde oxime	<i>X</i> rt	1.273 (4)	1.393 (4)	112.1 (3)	(q)
2-Ethoxy-isonitrosoacetanilide	<i>X</i> rt	1.289 (5)	1.396 (4)	111.6 (3)	(r)
1-Phenyl-1,2-propanedione 2-oxime	<i>X</i> rt	1.278 (5)	1.405 (5)	113.0 (3)	(s)
(±)-Carvoxime	<i>X</i> rt	1.286 (2)	1.410 (2)	112.9 (1)	(t)
Cyclohexane 1,4-dioxime	<i>X</i> rt	{ 1.275 (4)	1.409 (3)	110.7 (2)	(u)
		{ 1.277 (3)	1.413 (3)	112.0 (2)	
<i>E</i> -1-(2,4,6-trimethylphenyl)ethanone oxime	<i>X</i> rt	1.270 (3)	1.412 (3)	113.6 (3)	(v)
Cyclotetradecane oxime	<i>X</i> 113 K	{ 1.280 (3)	1.419 (2)	113.8 (2)	(w)
Cyclodecane oxime		{ 1.275 (2)	1.425 (1)	112.4 (1)	

References: (a) Coffey, Britt & Boggs (1968); (b) Talberg (1979); (c) Talberg (1978); (d) Talberg (1977a); (e) Dickinson, Kirby, Sweeny & Tyler (1973); (f) Cameron & Prout (1969); (g) Talberg (1976); (h) Talberg (1977b); (i) Talberg (1975); (j) Raston & White (1976); (k) Present work; (l) Talberg (1974); (m) Van Oijen & Romers (1966); (n) Van Havere, Lenstra, Geise, Van den Berg & Benschop (1982); (o) Bertolasi, Gilli & Veronese (1982); (p) Martínez-Ripoll & Lorenz (1976); (q) Martínez-Ripoll & Lorenz (1973); (r) Briansó, Miravittles, Plano & Font-Altaba (1973); (s) Saarinen, Korvenranta & Näsäkkälä (1977); (t) Oonk & Kroon (1976); (u) Groth (1968); (v) Fortier, Birnbaum, Buchanan & Dawson (1980); (w) Groth (1979).

(1977b), who was the first to draw this kind of plot, interpreted the curve as a hyperbola. Simple chemical considerations, however, show it can be accounted for in a different manner. Let us assume, according to Pauling (1960), that the π -bond order, n , is related to the shortening, Δd , of the single-bond distance by the equation $\Delta d = -c \log n$, where c is a constant to be determined. In the present case the double bond is distributed between the C—N and N—O bonds with $n_1 + n_2 = 1$, which leads to the equation*

$$10^{-\Delta d_1/c} + 10^{-\Delta d_2/c} = 1, \quad (1)$$

where $\Delta d_1 = d_{\text{CN}} - d_{\text{C=N}}$ and $\Delta d_2 = d_{\text{NO}} - d_{\text{N=O}}$ are the differences between the actual and pure double-bond distances. The best fit with the experimental values is obtained for $c = 0.30$, $d_{\text{C=N}} = 1.25$ and $d_{\text{N=O}} = 1.20$ Å. The dotted line in Fig. 3(a) corresponds to the curve calculated with these parameters. It is seen

* In principle, equation (1) could be written with two different values of the constant c as they refer to bonds which are different in nature (C—N and N—O). A single value has been adopted in view of the symmetrical form of the $d_{\text{N=O}}$ vs $d_{\text{C=N}}$ plot.

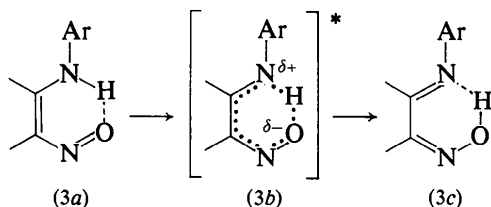
that the C—N and N—O π -bond orders are close to 0.5 for all bond situations corresponding or similar to that of an isonitroso ion (Table 2, references *h*, *i*, *j*, *k*), indicating that in these ions the double bond is symmetrically distributed between C—N and N—O bonds. The plot shows that C-nitroso compounds are spread out over a wider range of bond distances and orders than oximes, which appear to be relatively rigid. The empty zone centred at $(d_{\text{CN}}, d_{\text{NO}}) \simeq (1.31, 1.33)$ Å would correspond to the intermediate positioning of the proton, a point situated between C-nitroso compounds and oximes which is not actually attained.

Fig. 3(b) reports a scatter plot of C—N—O angles, $\alpha(\text{CNO})$, vs N—O distances for compounds of Table 2. The $\alpha(\text{CNO})$'s are confined in a narrow interval for oximes, without entertaining any apparent relationship with the N—O distances. Conversely, in C-nitroso compounds the angles range from 112.6 to 119.9° and are strongly correlated ($r = 0.93$) with the N—O, and then C—N, distances. A simple interpretation of this dependence can be given in terms of VSEPR (valence-shell electron pair repulsion) formalism (Gillespie, 1972). Long N—O distances correspond to increasing

contributions of the polar canonical form *1b*. The negative charge located on the oxygen cuts its electronegativity down causing an increase of the room taken up by the VSEP on the N-O bond.

The [1,5] sigmatropic rearrangement and its transition state

The asymmetric [1,5] sigmatropic rearrangement converting a nitroso vinylamine *3a* to an iminoxime *3c* through a hypothetical transition state *3b* is shown in the following scheme:



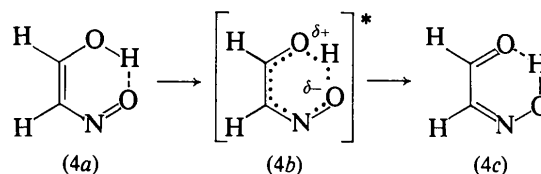
From the previous discussion, see schemes II*a,b*, it is clear that the bond situation in *3b* is not far from that experimentally found in II, differing mainly for the symmetrical positioning of the proton. Extending this concept, it is conceivable that the geometry of *3b* can be obtained by extrapolating curves of Figs. 3(*a*) and (*b*) beyond that of II in the direction of the oximes. The rearrangement *3a* → *3b* can be understood as a continuous approaching of the hydrogen to the nitroso oxygen, while the C-N-O geometry changes along curves of Figs. 3(*a*) and (*b*) from that of a pure C-nitroso compound to that of an oxime.

Taking this model for granted, it turns out that, while C-N and N-O distances change in a continuous way along the hypothetical reaction coordinate, the $\alpha(\text{CNO})$ vs d_{NO} curve shows a point of discontinuity. Assuming $d_{\text{NO}} \approx 1.33$ and $d_{\text{CN}} \approx 1.31$ Å for the transition state, the corresponding value for $\alpha(\text{CNO})$ should be $\approx 121^\circ$, a value which is not far from those obtained for the polar forms of C-nitroso compounds but is completely different from those observed in oximes. This is quite reasonable as it is known that oximes are more stable than C-nitroso derivatives and that the transformation is an exothermic process; thus the transition state should resemble more the higher-energy isomer, in agreement with the Hammond postulate (Hammond, 1955). On the other hand, it may well be that the $\alpha(\text{CNO})$ in *3c* is a few degrees wider than that represented by the cluster of points of Fig. 3(*b*), all making reference to antiperiplanar arrangements of the OH. In fact, no crystal structure of oximes of cyclic type *3c* is available for the great preference these compounds display for forming intermolecular hydro-

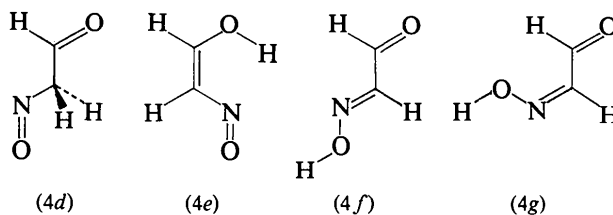
gen bonds of the type $=\text{N} \cdots \text{H}-\text{O} \cdots \text{N}=\text{O}$ (Bertolasi, Gilli

& Veronese, 1982).

This kind of reasoning is supported by theoretical *ab initio* calculations at the 4-31G level with full geometry optimization (Bouma & Radom, 1979) on the similar system describing the [1,5] sigmatropic hydrogen shift from nitrosovinyl alcohol *4a* to glyoxal monoxime *4c*



and related molecules *4d-4g*.



The optimized C-N-O geometries are reported by open triangles in Figs. 3(*a*) and (*b*). The agreement with the crystallographically determined values is quite good for C-nitroso compounds *4a*, *4d* and *4e* and oximes *4f* and *4g*, all in the ground state. Also, the geometry of *4c* can be considered substantially correct, in spite of the $\alpha(\text{CNO})$ value calculated some 5° wider than in the other oximes. The reason for this discrepancy has been discussed already and is believed to be the lack of structural data for α -diketomonoximes closing a ring by intramolecular hydrogen bonding as in *4c*. Conversely, there may be some doubts that the geometry of the transition state *4b* is properly calculated, as it seems to be too close to the C-nitroso geometry for both C-N-O distances and angles.

Such an agreement between fundamental-state geometries derived by methods so far apart as theoretical chemistry and X-ray crystallography seems to be encouraging. In general the agreement is continuously improving and this is due to increased flexibility of bases used for *ab initio* calculations, as pointed out recently by Cruickshank (1982). As far as the discrepancies on the transition states are concerned, we are inclined to think that they are due to a still imperfect theoretical treatment of these systems rather than to a fault in the method we have used in extrapolating them from structural data.

Table 3. Positional ($\times 10^4$ for non-hydrogen and $\times 10^3$ for hydrogens) and thermal ($\text{\AA}^2 \times 10^3$) parameters for compounds I and II, with e.s.d.'s in parentheses U_{eq} is as defined by Hamilton (1959).

	Compound I				Compound II				
	x	y	z	U_{eq}/U	x	y	z	U_{eq}/U	
C(1)	9968 (1)	8281 (3)	-1449 (2)	48 (1)	C(1)	7295 (2)	4988 (3)	1974 (2)	66 (2)
C(2)	9535 (1)	8930 (3)	-704 (3)	50 (2)	C(2)	8224 (2)	4544 (3)	2250 (1)	62 (2)
C(3)	9114 (2)	8415 (3)	174 (3)	48 (2)	C(3)	8543 (2)	4882 (3)	2920 (1)	52 (2)
C(4)	9117 (2)	7247 (2)	301 (2)	42 (1)	C(4)	7918 (2)	5672 (2)	3306 (1)	45 (1)
C(5)	9549 (2)	6605 (3)	-480 (3)	51 (2)	C(5)	6984 (2)	6112 (3)	3039 (1)	55 (2)
C(6)	9978 (2)	7117 (3)	-1351 (3)	56 (2)	C(6)	6683 (2)	5768 (3)	2365 (1)	68 (2)
C(7)	8189 (1)	7038 (2)	1927 (3)	46 (2)	C(7)	9032 (2)	6372 (2)	4309 (1)	43 (1)
C(8)	7881 (1)	6180 (2)	2771 (2)	43 (2)	C(8)	9071 (2)	6544 (2)	5050 (1)	45 (1)
C(9)	7335 (1)	6495 (2)	3655 (2)	46 (2)	C(9)	9998 (2)	7089 (2)	5411 (1)	53 (2)
C(10)	7032 (2)	5622 (3)	4509 (4)	62 (2)	C(10)	10896 (2)	7388 (3)	4981 (1)	56 (2)
C(11)	6584 (2)	7961 (4)	4633 (4)	68 (2)	C(11)	10644 (2)	7723 (2)	4216 (1)	46 (1)
N(1)	8711 (1)	6646 (2)	1182 (2)	45 (1)	C(12)	9966 (2)	6631 (3)	3907 (1)	48 (2)
N(2)	8071 (1)	5080 (2)	2868 (2)	49 (1)	C(13)	10094 (3)	9042 (3)	4157 (2)	59 (2)
N(3)	7110 (1)	7540 (2)	3748 (2)	54 (1)	C(14)	11635 (2)	7773 (4)	3827 (2)	66 (2)
O(1)	7972 (1)	8033 (2)	1916 (2)	70 (1)	N(1)	8159 (2)	5973 (2)	4021 (1)	47 (1)
O(2)	8585 (1)	4677 (2)	2194 (2)	57 (1)	N(2)	8311 (2)	6265 (2)	5472 (1)	59 (1)
Cl	10521 (1)	8964 (1)	-2508 (1)	76 (1)	O(1)	10037 (2)	7274 (2)	6036 (1)	82 (1)
H(N1)	882 (2)	597 (3)	133 (3)	56 (9)	O(2)	7451 (1)	5822 (2)	5197 (1)	68 (1)
H(N3)	732 (2)	809 (3)	327 (4)	77 (11)	H(N1)	761 (3)	589 (3)	439 (2)	95 (10)
H(2)	953 (1)	976 (3)	-81 (2)	44 (7)	H(1)	708 (2)	473 (3)	149 (2)	85 (9)
H(3)	883 (2)	886 (3)	70 (3)	69 (10)	H(2)	866 (2)	397 (3)	198 (1)	83 (10)
H(5)	952 (2)	586 (3)	-46 (4)	79 (12)	H(3)	920 (2)	450 (3)	314 (1)	66 (8)
H(6)	1027 (2)	666 (3)	-185 (3)	59 (9)	H(5)	653 (2)	667 (3)	333 (1)	55 (7)
H(101)	706 (2)	482 (4)	403 (4)	106 (14)	H(6)	606 (2)	607 (3)	217 (1)	78 (9)
H(102)	727 (2)	566 (4)	522 (4)	91 (13)	H(101)	1131 (2)	658 (3)	500 (1)	76 (9)
H(103)	650 (2)	582 (3)	468 (4)	97 (13)	H(102)	1129 (2)	809 (3)	520 (1)	75 (9)
H(111)	609 (2)	778 (3)	437 (4)	90 (12)	H(121)	1037 (2)	576 (3)	390 (1)	70 (8)
H(112)	660 (3)	874 (5)	480 (5)	118 (17)	H(122)	976 (2)	684 (2)	342 (1)	45 (6)
H(113)	668 (3)	764 (5)	536 (6)	123 (19)	H(131)	942 (2)	905 (3)	439 (1)	75 (9)
					H(132)	1053 (2)	978 (3)	435 (1)	88 (10)
					H(133)	995 (2)	925 (3)	364 (2)	71 (8)
					H(141)	1145 (2)	794 (3)	332 (2)	66 (8)
					H(142)	1208 (2)	844 (3)	401 (1)	79 (10)
					H(143)	1201 (3)	687 (3)	385 (2)	91 (10)

APPENDIX Experimental

The crystals used for X-ray analysis were small coloured prisms, the red one (I) having dimensions of $0.15 \times 0.30 \times 0.45$ mm and the blue-green one (II) of $0.15 \times 0.20 \times 0.06$ mm. Intensity data were collected on an automatic Siemens AED diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation and $\omega/2\theta$ scan technique ($\theta \leq 60^\circ$). For compound I 1759 independent reflections were collected, out of which 1588 having $I > 3\sigma(I)$ were considered observed. For II the number of independent reflections was 1658 with 1144 observed (3σ level). No absorption correction was made. Crystal data are given in the *Abstract*.

Both structures were solved by direct methods by means of *SHELX 76* (Sheldrick, 1976). H atoms were located from the difference maps calculated after the isotropic refinement. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Both structures were refined by full-matrix least squares assuming anisotropic temperature factors for all atoms but H's, which were refined isotropically. Weights were given according to the scheme $k_1/w = \sigma^2(F_o) + k_2|F_o|^2$, where k_1 and k_2 are constants to be

Table 4. Interatomic distances (\AA) with e.s.d.'s in parentheses

	I	II	I	II
C(1)-C(2)	1.372 (4)	1.380 (3)		
C(1)-C(6)	1.373 (4)	1.372 (2)	C(9)-N(3)	1.301 (3)
C(1)-Cl	1.740 (3)		C(9)-O(1)	1.215 (2)
C(2)-C(3)	1.378 (4)	1.381 (3)	C(10)-C(11)	1.532 (3)
C(3)-C(4)	1.381 (4)	1.383 (3)	C(11)-C(12)	1.526 (3)
C(4)-C(5)	1.391 (4)	1.378 (3)	C(11)-C(13)	1.524 (3)
C(4)-N(1)	1.411 (3)	1.430 (2)	C(11)-C(14)	1.521 (3)
C(5)-C(6)	1.379 (4)	1.384 (3)	C(11)-N(3)	1.457 (4)
C(7)-C(8)	1.483 (4)	1.436 (2)	N(2)-O(2)	1.290 (3)
C(7)-C(12)		1.492 (3)	N(1)-H(N1)	0.83 (3)
C(7)-N(1)	1.343 (3)	1.310 (2)	N(3)-H(N3)	0.91 (4)
C(7)-O(1)	1.236 (3)		N(1)...O(2)	2.579 (3)
C(8)-C(9)	1.445 (4)	1.477 (3)	O(2)...H(N1)	1.85 (3)
C(8)-N(2)	1.344 (3)	1.337 (2)	N(3)...O(1)	2.626 (3)
C(9)-C(10)	1.498 (4)	1.493 (3)	O(1)...H(N3)	1.92 (3)

determined. Final values of the discrepancy indices, R and $R_w = \sum w^{1/2} |A| / \sum w^{1/2} |F_o|$ were 0.053 and 0.056 for I, and 0.035 and 0.039 for II. Final atomic positional parameters are reported in Table 3.* Inter-

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38347 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Interatomic angles (°) with e.s.d.'s in parentheses*

	I	II		I	II
C(2)-C(1)-C(6)	121.0 (2)	120.0 (2)	C(8)-C(9)-N(3)	121.1 (2)	
C(2)-C(1)-Cl	118.7 (2)		C(8)-C(9)-O(1)		121.5 (2)
C(6)-C(1)-Cl	120.3 (2)		C(10)-C(9)-N(3)	118.7 (3)	
C(1)-C(2)-C(3)	119.9 (3)	120.2 (2)	C(10)-C(9)-O(1)		121.0 (2)
C(2)-C(3)-C(4)	120.4 (3)	119.0 (2)	C(9)-C(10)-C(11)		115.8 (2)
C(3)-C(4)-C(5)	118.7 (2)	121.3 (2)	C(10)-C(11)-C(12)		108.0 (2)
C(3)-C(4)-N(1)	124.4 (2)	122.0 (2)	C(10)-C(11)-C(13)		110.5 (2)
C(5)-C(4)-N(1)	116.9 (2)	116.5 (2)	C(10)-C(11)-C(14)		109.1 (2)
C(4)-C(5)-C(6)	121.2 (3)	118.8 (2)	C(12)-C(11)-C(13)		110.4 (2)
C(1)-C(6)-C(5)	118.8 (3)	120.7 (2)	C(12)-C(11)-C(14)		108.8 (2)
C(8)-C(7)-C(12)		119.7 (2)	C(13)-C(11)-C(14)		109.9 (2)
C(8)-C(7)-N(1)	114.8 (2)	117.0 (2)	C(7)-C(12)-C(11)		113.5 (2)
C(8)-C(7)-O(1)	121.9 (2)		C(4)-N(1)-C(7)	128.6 (2)	128.8 (2)
C(12)-C(7)-N(1)		123.3 (2)	C(4)-N(1)-H(N1)	119 (2)	121 (1)
N(1)-C(7)-O(1)	123.3 (2)		C(7)-N(1)-H(N1)	112 (2)	110 (1)
C(7)-C(8)-C(9)	120.7 (2)	120.5 (2)	C(8)-N(2)-O(2)	119.9 (2)	118.3 (1)
C(7)-C(8)-N(2)	127.3 (2)	125.4 (2)	C(9)-N(3)-C(11)	125.8 (3)	
C(9)-C(8)-N(2)	112.0 (2)	114.0 (2)	C(9)-N(3)-H(N3)	119 (2)	
C(8)-C(9)-C(10)	120.2 (3)	117.4 (2)	C(11)-N(3)-H(N3)	115 (2)	

Table 6. *Selected torsion angles (°) with e.s.d.'s in parentheses*

	I	II
C(3)-C(4)-N(1)-C(7)	9.8 (4)	47.8 (4)
N(1)-C(7)-C(8)-N(2)	0.5 (4)	3.8 (3)
C(7)-C(8)-N(2)-O(2)	1.5 (4)	-1.3 (3)
C(7)-C(8)-C(9)-N(3)	-1.3 (3)	
C(7)-C(8)-C(9)-O(1)		178.1 (2)

atomic distances and angles and a selection of torsion angles are given in Tables 4, 5 and 6 respectively.

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