

along **b** (the shortest parameter) with H...O distances less than the sum of the van der Waals radii. Similar contacts have been observed in DL-homocystine and DL-homocystine monohydrogen oxalate. Also, the methylene group (C<sup>δ</sup>H<sub>2</sub>) is involved in a short intermolecular C—H...O contact and the value of the H—C...O'' angle falls in the range 22–59° observed by Sutor (1962) for this kind of interaction.

The N atoms around Cl form a distorted square-pyramidal arrangement with the chloride ion displaced by 0.349 (2) Å towards the top of the pyramid, the base of which is formed by N(1), N(1<sup>ii</sup>), N(2), N(2<sup>ii</sup>). The additional long contact Cl...S(1) = 3.618 (3) Å makes the environment severely distorted octahedral.

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## Structures of *E,E*-3-(*p*-Tolylimino)-2-butanone Oxime and *E,Z*-4-(*p*-Tolylimino)-2,3-pentanedione 3-Oxime. An X-ray Crystallographic Investigation on Bonding in Oximes

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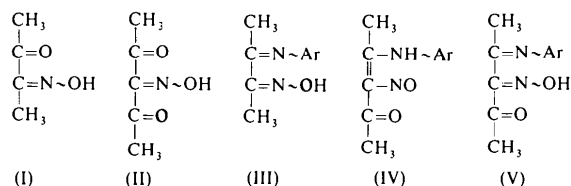
#### Abstract

Single-crystal X-ray analyses of *E,E*-3-(*p*-tolylimino)-2-butanone oxime (HIB) and *E,Z*-4-(*p*-tolylimino)-2,3-pentanedione 3-oxime (HIOP) are reported. HIB (C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O, *M<sub>r</sub>* = 190.25) crystallizes in space group *B*2<sub>1</sub>/*c* with *a* = 19.539 (4), *b* = 19.673 (4), *c* = 11.242 (3) Å, β = 92.80 (3)°, *Z* = 16, *D<sub>c</sub>* = 1.17 Mg m<sup>-3</sup>, μ(Cu *K*α) = 0.537 mm<sup>-1</sup>. HIOP (C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>, *M<sub>r</sub>* = 218.26) is orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with *a* = 7.296 (2), *b* = 14.747 (3), *c* = 11.177 (3) Å, *Z* = 4, *D<sub>c</sub>* = 1.20 Mg m<sup>-3</sup>, μ(Cu *K*α) = 0.600 mm<sup>-1</sup>. The structures were refined from diffractometer data and final *R* values were 0.045 (2610 observed reflections)

and 0.048 (1004 observed reflections) for HIB and HIOP respectively. Both molecules display the group Ar—N=C(*R*)—C(*R'*)=N—OH and the structure analyses show that they have opposite configurations at the two centres of *syn/anti* isomerism and differ in conformation as far as the rotation around the C—C single bond is concerned. The different conformations are discussed in terms of balance of π-bond delocalization and nonbonded intramolecular potential energies. A comparison of the present data with those of the literature allows a classification of hydrogen bonds in crystals of oximes, and a possible relation between hydrogen bonding and N—O bond distances is suggested.

## Introduction

Condensation products of 2,3-butanedione 3-oxime (I) and 2,3,4-pentanetrione 3-oxime (II) with *p*-toluidine are currently being investigated in our laboratories along with related vicinal multifunctional compounds (Veronese, Cavicchioni, D'Angeli & Bertolasi, 1981; Veronese & D'Angeli, 1979). Whereas spectroscopic data of the former compound point to the imino-hydroxyimino structure (III) in different solvents, <sup>1</sup>H NMR spectra of the latter reveal the presence of different species in equilibrium; these were tentatively identified as the nitroso-enaminone (IV) and the imino-hydroxyimino-ketone (V). The crystal structure determinations presently reported ascertained the structures and configurations of HIB and HIOP, in agreement with the proposed formulae (III) and (V).



## Experimental

The crystals used for X-ray analysis were small prisms of dimensions 0.24 × 0.24 × 0.36 mm for HIB and 0.40 × 0.17 × 0.60 mm for HIOP. Intensity data were collected on an automatic Siemens AED diffractometer with Ni-filtered Cu K $\alpha$  radiation and the  $\omega/2\theta$  scan technique ( $\theta \leq 60^\circ$ ). Both crystals were stable during the data-collection time. For HIB 3145 independent reflections were collected, out of which 2610 reflections having  $I \geq 3\sigma(I)$  were considered observed. For HIOP the number of independent reflections was 1022 with 1004 observed ( $3\sigma$  level). Lorentz and polarization corrections were applied as usual but no absorption correction was made. Crystal data are given in the *Abstract*. [For HIB the standard space group is  $P2_1/c$  with  $a = 11.507$  (2),  $b = 19.673$  (4),  $c = 11.242$  (3) Å,  $\beta = 122.00$  (4) $^\circ$ ,  $Z = 8$ .]

Both structures were solved by direct methods; that of HIB by *SHELX* 76 (Sheldrick, 1976) and that of HIOP by means of *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Most of the subsequent calculations were carried out by *SHELX* 76. Scattering factors were taken from *International*

Table 1. Positional parameters ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for the two independent molecules of HIB, with *e.s.d.*'s in parentheses

For non-hydrogen atoms  $U_{\text{eq}}$  is as defined by Hamilton (1959).

	Molecule A				Molecule B			
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U$	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U$
C(1)	4404 (1)	4114 (1)	2737 (2)	49 (1)	2921 (1)	-921 (1)	5224 (2)	52 (1)
C(2)	4230 (1)	4738 (1)	3208 (2)	56 (1)	2363 (1)	-1058 (2)	4465 (2)	74 (2)
C(3)	4544 (1)	5323 (1)	2819 (2)	61 (1)	2001 (1)	-526 (2)	3933 (2)	82 (2)
C(4)	5031 (1)	5305 (1)	1968 (2)	62 (1)	2188 (1)	142 (1)	4116 (2)	71 (2)
C(5)	5192 (1)	4677 (1)	1501 (2)	69 (2)	2761 (1)	267 (1)	4839 (2)	66 (2)
C(6)	4881 (1)	4089 (1)	1866 (2)	60 (1)	3124 (1)	-256 (1)	5393 (2)	58 (1)
C(7)	5367 (2)	5942 (2)	1539 (3)	92 (2)	1780 (2)	727 (3)	3555 (5)	112 (3)
C(8)	4184 (1)	3249 (1)	4110 (2)	47 (1)	3257 (1)	-1607 (1)	6870 (2)	51 (1)
C(9)	4683 (1)	3542 (1)	5028 (2)	63 (2)	2820 (2)	-1214 (1)	7694 (2)	64 (2)
C(10)	3798 (1)	2634 (1)	4429 (2)	48 (1)	3654 (1)	-2195 (1)	7346 (2)	56 (1)
C(11)	3296 (2)	2308 (2)	3566 (2)	70 (2)	4179 (3)	-2538 (2)	6641 (4)	101 (2)
N(1)	4069 (1)	3500 (1)	3066 (1)	49 (1)	3301 (1)	-1476 (1)	5754 (1)	55 (1)
N(2)	3922 (1)	2429 (1)	5496 (1)	53 (1)	3498 (1)	-2392 (1)	8386 (1)	60 (1)
O(1)	3533 (1)	1866 (1)	5781 (1)	63 (1)	3873 (1)	-2959 (1)	8759 (2)	76 (1)
H(1)	3658 (15)	1769 (14)	6528 (29)	106 (10)	3690 (15)	-3088 (15)	9449 (28)	108 (10)
H(2)	3877 (11)	4742 (10)	3785 (19)	61 (6)	2234 (13)	-1528 (13)	4322 (23)	90 (8)
H(3)	4415 (10)	5741 (11)	3176 (19)	61 (6)	1619 (13)	-615 (12)	3492 (22)	81 (8)
H(5)	5567 (13)	4645 (12)	901 (23)	82 (8)	2902 (12)	764 (13)	5001 (21)	83 (8)
H(6)	5033 (11)	3629 (11)	1534 (19)	65 (6)	3519 (12)	-151 (11)	5903 (20)	66 (7)
H(71)	5094 (19)	6157 (19)	918 (37)	143 (15)	1319 (21)	613 (21)	3584 (35)	153 (17)
H(72)	5405 (16)	6256 (17)	2111 (29)	115 (13)	1781 (23)	714 (23)	2699 (49)	194 (21)
H(73)	5752 (20)	5892 (21)	1108 (38)	152 (18)	1928 (26)	1146 (27)	3778 (46)	203 (28)
H(91)	4938 (12)	3182 (12)	5484 (22)	81 (8)	2678 (14)	-1528 (14)	8289 (26)	102 (9)
H(92)	5026 (12)	3858 (13)	4676 (21)	78 (7)	3064 (17)	-887 (17)	8073 (31)	126 (13)
H(93)	4432 (15)	3750 (15)	5589 (28)	107 (10)	2400 (16)	-1024 (16)	7294 (28)	122 (11)
H(111)	3518 (22)	2166 (23)	2732 (48)	207 (19)	4602*	-2684*	7242*	140*
H(112)	3142 (17)	1906 (19)	3800 (32)	136 (14)	3978 (23)	-2923 (25)	6285 (41)	170 (21)
H(113)	3049 (19)	2609 (20)	3196 (35)	141 (15)	4385 (14)	-2256 (16)	6093 (28)	110 (10)

\* Constrained parameters.

Table 2. *Positional parameters* ( $\times 10^4$ ) and *isotropic thermal parameters* ( $\text{\AA}^2 \times 10^3$ ) for *HIOP*, with *e.s.d.'s* in parentheses

For non-hydrogen atoms  $U_{eq}$  is as defined by Hamilton (1959).

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U$
C(1)	5513 (3)	-524 (1)	7360 (2)	41 (1)
C(2)	7079 (5)	-628 (2)	6679 (3)	59 (2)
C(3)	8631 (4)	-1010 (2)	7172 (3)	62 (2)
C(4)	8669 (4)	-1307 (2)	8359 (3)	50 (2)
C(5)	7081 (4)	-1226 (2)	9013 (3)	52 (2)
C(6)	5506 (4)	-844 (2)	8527 (2)	48 (1)
C(7)	10378 (5)	-1681 (2)	8910 (4)	69 (2)
C(8)	3230 (4)	586 (2)	7298 (2)	43 (1)
C(9)	1539 (5)	1014 (2)	6795 (3)	61 (2)
C(10)	4077 (4)	1083 (1)	8323 (2)	41 (1)
C(11)	5679 (5)	1678 (2)	8052 (2)	55 (2)
C(12)	6485 (8)	2241 (3)	9020 (4)	86 (3)
N(1)	3911 (3)	-131 (1)	6841 (2)	44 (1)
N(2)	3489 (3)	1068 (1)	9409 (2)	46 (1)
O(1)	1988 (3)	498 (1)	9517 (2)	54 (1)
O(2)	6261 (4)	1694 (2)	7038 (2)	88 (2)
H(1)	1619 (76)	467 (30)	10210 (56)	115 (17)
H(2)	7045 (50)	-433 (22)	5915 (41)	71 (9)
H(3)	9750 (59)	-1079 (23)	6707 (35)	71 (10)
H(5)	7074 (56)	-1467 (21)	9802 (34)	61 (9)
H(6)	4337 (48)	-752 (21)	9003 (29)	53 (8)
H(71)	11106 (91)	-2081 (40)	8439 (54)	129 (19)
H(72)	9920 (90)	-2108 (32)	9721 (52)	126 (17)
H(73)	11208 (96)	-1319 (47)	9056 (61)	131 (23)
H(91)	639 (65)	1102 (29)	7417 (41)	95 (12)
H(92)	1115 (70)	698 (30)	6089 (49)	96 (13)
H(93)	1917 (86)	1583 (41)	6533 (53)	133 (19)
H(121)	7015 (87)	1942 (34)	9538 (48)	100 (17)
H(122)	5364*	2587*	9456*	116*
H(123)	7308 (94)	2644 (35)	8685 (55)	123 (17)

\* Constrained parameters.

calculated position. At convergence, the  $R$  and  $R_w$  factors were, respectively, 0.048 and 0.047. The weighting scheme was the same as in the previous case.

Final atomic positional parameters are reported in Tables 1 and 2.\*

### Description of the structures

Both crystal structures consist of a van der Waals packing of linear infinite chains of molecules linked by hydrogen bonds (Figs. 1 and 2). In HIB there are two parallel systems of chains, one for each independent molecule of the asymmetric unit. In each chain hydrogen bonds  $O(1)-H(1)\cdots N(1)$  [ $O(1)-N(1) = 2.820(3)$  or  $2.786(3)$  Å;  $H(1)-N(1) = 1.94(4)$  or  $1.89(4)$  Å for molecules *A* and *B* respectively] connect two adjacent molecules related by the glide at  $y = \frac{1}{4}$  parallel to  $(x,z)$  and having translation of  $c/2$ . In HIOP the chains also run along  $c$ , but two adjacent molecules, linked by the hydrogen bond  $O(1)-H(1)\cdots N(1)$  [ $O(1)-N(1) = 2.734(5)$  and  $H(1)-N(1) = 1.93(8)$  Å] are related by a  $2_1$  axis parallel to  $c$  at  $x = \frac{1}{4}$  and  $y = 0$ .

Figs. 3 and 4 are *ORTEP* (Johnson, 1971) views of HIB (molecule *A*) and HIOP respectively. Bond distances and angles are reported in Tables 3 and 4. A selection of torsion angles is given in Table 5.

\* 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 36226 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

*Tables for X-ray Crystallography* (1974). All non-hydrogen atoms were found in the  $E$  maps corresponding to the highest values of the combined figure of merit.

HIB was refined by blocked-matrix (two blocks, one for each independent molecule of the asymmetric unit) least squares by assuming anisotropic temperature factors for all atoms but H, which were refined isotropically. The methyl H(111) atom, bonded to C(11) of molecule *B*, was not found in the difference map and was assigned a calculated position. 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 determined. Final values of the discrepancy indices,  $R = \sum |A|/\sum |F_o|$  and  $R_w = \sum w^{1/2}|A|/\sum w^{1/2}|F_o|$ , were 0.045 and 0.049 respectively.

For HIOP the structure was refined by full-matrix least squares in the anisotropic mode for all C, N and O atoms and in the isotropic mode for H. The methyl hydrogen H(122) was found in the difference map but disappeared during the refinement. Thus it was given a

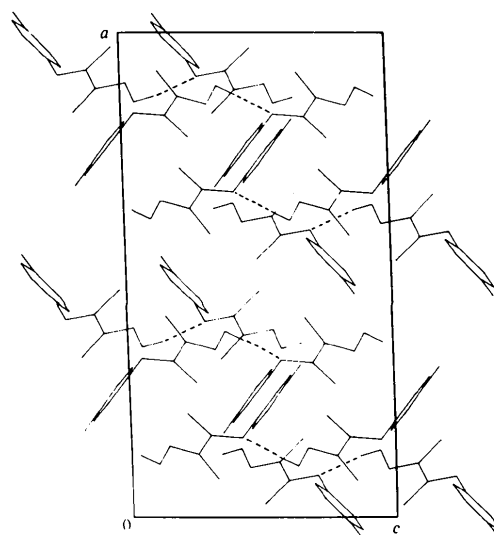


Fig. 1. The crystal packing of HIB molecules, as projected along the  $b$  axis.

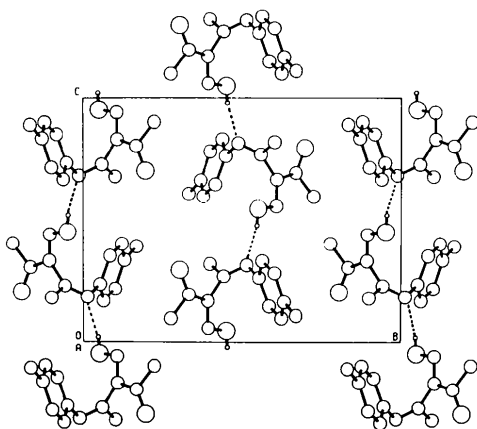


Fig. 2. The crystal packing of HIOP molecules, as projected along the *a* axis.

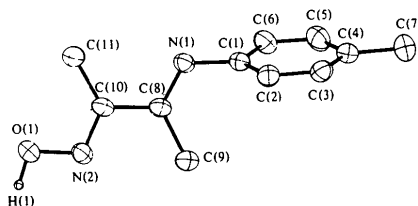


Fig. 3. Molecule of HIB(4), illustrating the thermal ellipsoids at 40% probability (Johnson, 1971).

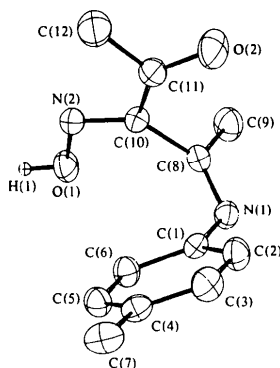


Fig. 4. Molecule of HIOP, illustrating the thermal ellipsoids at 40% probability (Johnson, 1971).

Both compounds have two centres of *syn/anti* isomerism related to the presence of the  $N(1)=C(8)$  and  $N(2)=C(10)$  double bonds. With respect to these, HIB is the *syn*-methyl, *syn*-methyl isomer and HIOP is the *anti*-methyl, *anti*-acetyl isomer or, in other words, the centres have the opposite configuration in the two compounds. They differ also in conformation as far as the rotation around the  $C(8)-C(10)$  single bond is concerned. The values of the torsion angles  $N(1)-C(8)-C(10)-N(2)$ ,  $-177.6(2)$  and  $-167.0(2)^\circ$  for HIB (molecules *A* and *B*) and  $-104.8(3)^\circ$  for HIOP, show that delocalization of  $\pi$  electrons throughout the heterodiene group

Table 3. Bond distances ( $\text{\AA}$ ) for HIOP and for the two independent molecules of HIB, with e.s.d.'s in parentheses

	HIOP	HIB(A)	HIB(B)
C(1)-C(2)	1.381 (6)	1.385 (3)	1.377 (3)
C(1)-C(6)	1.387 (5)	1.386 (3)	1.378 (3)
C(1)-N(1)	1.428 (4)	1.431 (3)	1.434 (3)
C(2)-C(3)	1.380 (7)	1.385 (3)	1.382 (4)
C(3)-C(4)	1.398 (6)	1.383 (3)	1.378 (4)
C(4)-C(5)	1.376 (6)	1.384 (3)	1.373 (3)
C(4)-C(7)	1.495 (6)	1.504 (5)	1.519 (6)
C(5)-C(6)	1.390 (6)	1.377 (3)	1.380 (3)
C(8)-C(9)	1.495 (6)	1.499 (3)	1.504 (3)
C(8)-C(10)	1.493 (5)	1.480 (3)	1.478 (3)
C(8)-N(1)	1.274 (4)	1.283 (2)	1.288 (2)
C(10)-C(11)	1.493 (6)	1.489 (3)	1.488 (5)
C(10)-N(2)	1.288 (4)	1.278 (2)	1.282 (3)
C(11)-C(12)	1.486 (6)		
C(11)-O(2)	1.210 (5)		
N(2)-O(1)	1.386 (4)	1.390 (2)	1.389 (2)
O(1)-H(1)	0.82 (8)	0.88 (3)	0.91 (3)

Table 4. Interatomic angles ( $^\circ$ ) for HIOP and for the two independent molecules of HIB, with e.s.d.'s in parentheses

	HIOP	HIB(A)	HIB(B)
C(2)-C(1)-C(6)	118.9 (3)	119.2 (2)	119.0 (2)
C(2)-C(1)-N(1)	119.9 (3)	121.7 (2)	119.2 (2)
C(6)-C(1)-N(1)	121.1 (3)	119.0 (2)	121.7 (2)
C(1)-C(2)-C(3)	120.2 (4)	119.7 (2)	119.6 (3)
C(2)-C(3)-C(4)	121.6 (4)	121.8 (2)	122.0 (3)
C(3)-C(4)-C(5)	117.4 (4)	117.5 (2)	117.6 (2)
C(3)-C(4)-C(7)	121.6 (4)	121.8 (2)	122.0 (3)
C(5)-C(4)-C(7)	121.1 (4)	120.8 (2)	120.4 (3)
C(4)-C(5)-C(6)	121.6 (4)	121.7 (2)	121.3 (2)
C(1)-C(6)-C(5)	120.1 (4)	120.1 (2)	120.5 (2)
C(9)-C(8)-C(10)	115.0 (3)	118.0 (2)	118.9 (2)
C(9)-C(8)-N(1)	121.4 (3)	124.2 (2)	124.4 (2)
C(10)-C(8)-N(1)	123.6 (3)	117.8 (2)	116.8 (2)
C(8)-C(10)-C(11)	117.2 (3)	121.4 (2)	121.7 (2)
C(8)-C(10)-N(2)	125.3 (3)	114.1 (2)	115.0 (2)
C(11)-C(10)-N(2)	117.5 (3)	124.4 (2)	123.3 (2)
C(10)-C(11)-C(12)	119.4 (4)		
C(10)-C(11)-O(2)	118.4 (3)		
C(12)-C(11)-O(2)	122.1 (4)		
C(1)-N(1)-C(8)	119.5 (3)	119.9 (2)	119.9 (2)
C(10)-N(2)-O(1)	110.8 (3)	112.7 (2)	111.8 (2)
N(2)-O(1)-H(1)	112 (5)	105 (2)	105 (2)

$N(1)=C(8)-C(10)=N(2)$  is likely to occur only in HIB, where all the group is nearly planar, but not in HIOP, where the two double bonds lie on approximately orthogonal planes. In this latter compound the  $N(2)=C(10)$  double bond is nearly coplanar with that of the acetyl group [ $N(2)-C(10)-C(11)-O(2) = 179.3(3)^\circ$ ]. The phenyl ring is roughly perpendicular to the  $C(1), N(1), C(8)$  plane in both compounds (see Table 5), suggesting that the phenyl  $\pi$  orbitals are decoupled from the  $\pi$  system of the  $C=N$  double bonds.

Bond distances and angles are rather similar in the two compounds, with the exception of the angles at the

Table 5. A selection of torsion angles (°) for HIOP and the two independent molecules of HIB, with *e.s.d.*'s in parentheses

	HIOP	HIB(A)	HIB(B)
C(2)–C(1)–N(1)–C(8)	–121.1 (3)	–71.4 (3)	107.9 (2)
C(6)–C(1)–N(1)–C(8) = T1	61.9 (3)	113.1 (2)	76.3 (3)
C(1)–N(1)–C(8)–C(9)	–179.1 (2)	–2.9 (3)	0.4 (3)
C(1)–N(1)–C(8)–C(10)	3.6 (4)	176.8 (2)	178.9 (2)
N(1)–C(8)–C(10)–N(2) = T2	–104.8 (3)	–177.6 (2)	–167.0 (2)
N(1)–C(8)–C(10)–C(11)	78.2 (3)	0.7 (3)	11.3 (4)
C(9)–C(8)–C(10)–N(2)	77.8 (3)	2.2 (3)	11.6 (3)
C(9)–C(8)–C(10)–C(11)	–99.2 (3)	–179.6 (2)	–170.1 (3)
C(8)–C(10)–C(11)–O(2)	–3.5 (4)		
C(8)–C(10)–C(11)–C(12)	175.4 (3)		
C(8)–C(10)–N(2)–O(1)	2.2 (3)	177.8 (2)	177.9 (2)
N(2)–C(10)–C(11)–O(2) = T3	179.3 (3)		
N(2)–C(10)–C(11)–C(12)	–1.8 (4)		
C(11)–C(10)–N(2)–O(1)	179.1 (2)	–0.5 (3)	–0.3 (3)
C(10)–N(2)–O(1)–H(1)	178 (4)	–180 (2)	–173 (2)

C(8) and C(10) atoms. The N(1)–C(8)–C(10) angle is larger in HIOP (123.6°) than in HIB (average 117.3°), while the other two angles at C(8) decrease accordingly; this seems to be consistent with the changes in the pattern of nonbonded interaction among the atoms involved. A similar effect is observed for the angles at C(10): N(2)–C(10)–C(8) is 125.3° in HIOP and only 114.6° (average) in HIB, while the other two adjacent angles change in the opposite direction. In this case the widening of the N(2)–C(10)–C(8) angle seems to be more easily interpretable in terms of decreased VSEPR (valence shell electron pair repulsion; Gillespie, 1970) as a consequence of the substitution of the methyl by the more electron-withdrawing acetyl group.

The C(8)–C(10) distance is slightly shorter in HIB [average 1.479 (3) Å] than in HIOP [1.493 (5) Å], in agreement with the idea of a partial double-bond contribution in planar HIB, but the difference of 3.5σ is barely significant. In general, the shortening of the C<sub>sp</sub>–C<sub>sp<sup>2</sup></sub> single-bond distance caused by conjugation appears to be too small, in dienic systems, to be considered a convincing proof of the conjugation itself. In fact, only in glyoxime (Calleri, Ferraris & Viterbo, 1966) was this distance [1.449 (6) Å] found to be significantly shorter than the theoretical C<sub>sp</sub>–C<sub>sp<sup>2</sup></sub> single-bond value of 1.48 Å, but in other oximes having coplanar conjugated double bonds it was found to lie in the interval 1.47–1.50 Å (Briansó, Miravittles, Plana & Font-Altaba, 1973; Saarinen, Korvenranta & Näsäkkälä, 1977; Allen, Trotter & Rogers, 1970; Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1973). On the other hand, gas electron diffraction studies on planar substituted butadienes or hexatrienes have also failed to find significant shrinkages of the C<sub>sp</sub>–C<sub>sp<sup>2</sup></sub> single bond (Trætterberg, 1968; Aten, Hedberg & Hedberg, 1968).

The geometry of the oxime moiety is strictly similar in the two compounds. The N–O distances and

C=N–O angles of 1.390 (2), 1.389 (2), 1.386 (4) Å and 112.7 (2), 111.8 (2) and 110.8 (3)° in HIB (molecules A and B) and HIOP, respectively, fall in the middle of the accepted ranges for these quantities (*i.e.* 1.36–1.44 Å and 109–116°). It may be of interest to point out the difference between the C=N–C angles at the N(1) imino nitrogen (all very close to 120°) and the C=N–O angles at the N(2) oxime nitrogen (111–112°), although both N atoms should correspond to the same *sp*<sup>2</sup> hybridization. The simplest explanation of this difference can again be given in terms of VSEPR theory, as a smaller angular space can be allocated to the N–O bond in view of the higher electronegativity of the O atom and the bulky lone pair can be identified most properly as the leading force of the angular change.

## Discussion

The simultaneous presence of several functional groups and of conjugated double bonds gives rise to different orders of problems in the interpretation of the molecular structures of these compounds. The discussion has been restricted to the following points: (i) conjugation in the heterodiene system; (ii) intra- and intermolecular hydrogen-bond (HB) formation in oxime crystals; (iii) geometry of the oxime group.

We have already remarked that the observed changes of bond distances are unable to detect double-bond contribution to the C<sub>sp</sub>–C<sub>sp<sup>2</sup></sub> single bond. On the other hand, dienic and heterodiene systems are often found in planar conformations, which is indicative of such a partial double-bond character. More insight into the problem can be gained by minimizing the nonbonded intramolecular potential energy, *U*, of the free molecules by the use of atom–atom potentials (Giglio, 1969) and checking whether or not the minimum corresponds to the conformation observed in the crystal. Two torsion angles were allowed to change, *i.e.* T1 = C(6)–C(1)–N(1)–C(8) and T2 = N(1)–C(8)–C(10)–N(2), the remaining angles being constrained to their crystal values; methyl groups were considered as single atoms with appropriate potentials. The maps *U*(T1, T2) for HIB (molecule B) and HIOP are shown in Figs. 5 and 6. The absolute minima are found at (91.0, –93.8°) for HIB and (91.9, –92.2°) for HIOP and these values are marked on the maps together with the corresponding experimental values. The observed and calculated values are in fairly good agreement (within 1 kcal mol<sup>–1</sup>) for HIOP. In HIB only the conformation of the phenyl ring is found to correspond to a minimum of nonbonded intramolecular energy, while a complete disagreement between calculated and observed conformations is observed as far as the rotation around the C(8)–C(10) single bond is concerned. This can be explained in

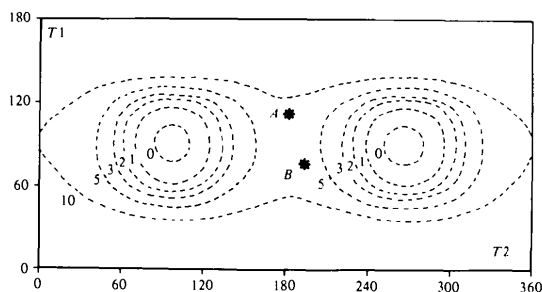


Fig. 5. Intramolecular potential energy in kcal mol<sup>-1</sup> (1 kcal mol<sup>-1</sup> ≡ 4.2 kJ mol<sup>-1</sup>) calculated for HIB (molecule *B*) as a function of the torsion angles  $T_1 = C(6)-C(1)-N(1)-C(8)$  and  $T_2 = N(1)-C(8)-C(10)-N(2)$ . Experimental minima are indicated by stars.

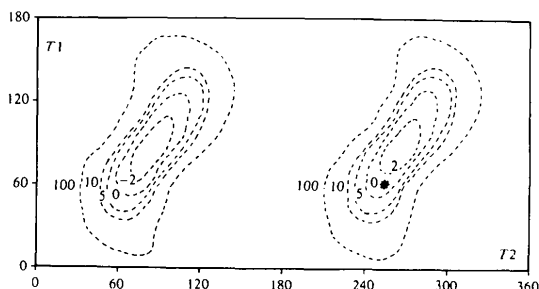


Fig. 6. The same intramolecular potential energy map as in Fig. 5, but calculated for HIOP.

terms of the balance of two different forces, one arising from the double-bond contribution to the  $=C-C=$  bond, which tends to flatten the molecule, and the other from the steric hindrance of the substituents, which induces a mutually perpendicular arrangement of the two moieties. In HIOP the barrier arising from nonbonded interactions alone is so great that the two moieties are compelled to be orthogonal, while in HIB this barrier is far smaller and can be overcome by the gain in energy ensuing from partial delocalization of the  $\pi$  system. Strictly similar arguments can be used for hinting at the double-bond contribution to the  $C(10)-C(11)$  single bond of the acetyl group in HIOP, although the observed distance of 1.493 (6) Å does not differ from the accepted value of 1.48 Å for a pure  $C_{sp^2}-C_{sp^2}$  single bond. In fact the observed value of torsion angle  $T_3 = N(2)-C(10)-C(11)-O(2)$  is 179.3°, while the minimum of the nonbonded interaction energy is located at  $T_3 = 92.9^\circ$ .

Table 6 reports the essential geometrical parameters of 57 oxime groups, as determined by the 46 most recent crystal analyses. No screening of the available data has been done and only a few crystal structure determinations of very low quality have been omitted.

The column headed 'HB' reports the types of hydrogen bonds observed in the crystals and the meaning of codes 1, 2 and 3 is illustrated in Fig. 7. HB

of type 1, where the oxime OH is a HB donor, is formed by all the 57 groups investigated, while the oxime nitrogen is a HB acceptor (type 2) in 35 groups, in which case  $X_2=X_1$  and HB's 1 and 2 coincide.\* This gives rise to a typical crystal packing built up of dimers closing the six-membered ring  $=C=N \cdots O-H \cdots N=C=$ , although a small number of other packings (such as trimers, chains or planes) have been reported. Values of  $N \cdots X_2$  distances for HB's of type 2 are also shown in Table 6.

An analysis of the 15 cases where  $X_1$  is different from the oxime N seems to indicate that this situation is associated with the presence in the molecule of N or O atoms having a net atomic charge more negative than the oxime N itself. This can be easily shown for the present compounds and Fig. 8 reports the values of the net atomic charges and HOMO electron densities calculated by semi-empirical quantum-mechanical methods in the INDO (Pople & Beveridge, 1970) approximation on the basis of the experimental geometries with calculated H positions. Both quantities agree in indicating that N(1) is a better HB acceptor

\* This last rule is broken only by samples (32) and (33), where the  $N \cdots H-X_2$  hydrogen bond is intramolecular.

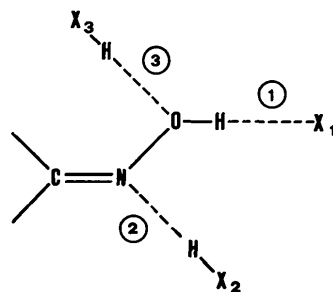


Fig. 7. The three types of hydrogen bonds formed by oxime groups in crystals.

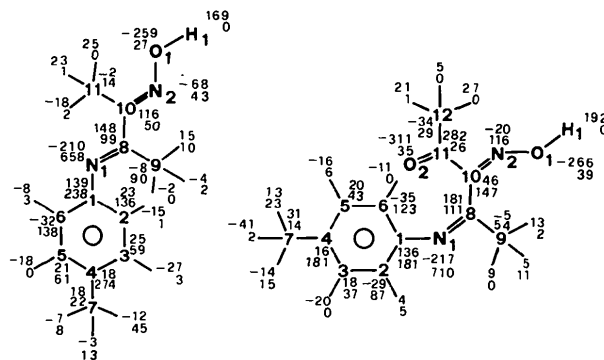


Fig. 8. Net atomic charges (upper figures) and HOMO electron densities (lower figures) calculated for HIB (molecule *B*) and HIOP in the INDO (Pople & Beveridge, 1970) approximation (units of  $10^{-3}$  electrons).

Table 6. Geometrical parameters of 57 oxime groups as determined in 46 crystal analyses

N—O and C=N bond distances and N...X<sub>2</sub> hydrogen-bond distances are in Å and C=N—O angles in degrees (e.s.d.'s in parentheses). The column HB reports the codes, explained in Fig. 7, of the hydrogen bonds formed by each oxime group. Symbols DD, D, Ar and — in column CONJN correspond to the bonding situations =C=C=C=C=NOH, =C=C=NOH, Ar—C=NOH and R—C=NOH respectively; the symbol / indicates a decoupling of the π systems caused by a rotation of more than 20° around the C—C single bond. Underlined N...X<sub>2</sub> distances correspond to intramolecular hydrogen bonds.

	HB	CONJN	N—O	C=N	C=N—O	N...X <sub>2</sub>	X <sub>2</sub>	Reference
(1)	1	DD	1.365 (7)	1.306 (7)	112.5 (7)			(a)
(2a)	1	DD	1.362 (3)	1.310 (3)	112.3 (2)			(b)
(2b)	1	DD	1.371 (3)	1.302 (3)	112.8 (1)			(b)
(3)	1	Ar	1.378 (7)	1.285 (8)	114.0 (5)			(c)
(4)	1	Ar	1.375 (3)	1.278 (3)	114.2 (2)			(d)
(5)	1	Ar	1.379 (2)	1.268 (2)	115.5 (1)			(e)
(6)	1	Ar	1.390 (7)	1.275 (8)	111.1 (5)			(f)
(7)	1	D	1.381 (9)	1.27 (1)	112.2 (6)			(g)
(8a)	1	D	1.389 (2)	1.282 (3)	111.8 (2)			(h)
(8b)	1	D	1.390 (2)	1.278 (2)	112.7 (2)			(h)
(9)	1	D	1.386 (4)	1.288 (4)	110.8 (3)			(i)
(10)	1	Ar	1.393 (4)	1.273 (4)	112.1 (3)			(j)
(11a)	1	D	1.400 (3)	1.289 (4)	112.5 (3)			(k)
(11b)	1	D	1.404 (3)	1.289 (4)	111.8 (3)			(k)
(12)	1	D	1.396 (4)	1.289 (5)	111.6 (3)			(l)
(13)	1	—	1.403 (5)	1.259 (5)	111.7 (3)			(m)
(14)	1	D	1.407 (3)	1.267 (4)	111.7 (3)			(n)
(15)	1	Ar/	1.418 (4)	1.276 (4)	112.9 (3)			(o)
(16)	1 + 2	D	1.38 (1)	1.31 (1)	112.8 (7)	2.81	O	(p)
(17)	1 + 2	Ar/	1.392 (8)	1.297 (9)	114.2 (6)	2.78	O	(q)
(18)	1 + 2	Ar	1.395 (6)	1.284 (7)	113.1 (4)	2.77	O	(r)
(19a)	1 + 2	—	1.390 (7)	1.276 (7)	113.7 (5)	2.81	O	(s)
(19b)	1 + 2	—	1.391 (7)	1.288 (7)	113.7 (5)	2.79	O	(s)
(19c)	1 + 2	—	1.407 (7)	1.273 (7)	112.1 (5)	2.80	O	(s)
(19d)	1 + 2	—	1.411 (7)	1.258 (7)	112.9 (5)	2.78	O	(s)
(19e)	1 + 2	—	1.414 (7)	1.272 (7)	111.9 (5)	2.78	O	(s)
(19f)	1 + 2	—	1.426 (7)	1.307 (7)	109.3 (5)	2.72	O	(s)
(20)	1 + 2	D	1.397 (4)	1.284 (5)	111.0 (3)	2.81	O	(t)
(21)	1 + 2	D	1.394 (3)	1.284 (3)	111.5 (2)	2.87	O	(u)
(22)	1 + 2	D	1.393 (4)	1.281 (4)	111.4 (3)	3.08	N	(v)
(23)	1 + 2	D	1.410 (2)	1.286 (2)	112.9 (1)	2.80	O	(w)
(24)	1 + 2	Ar	1.408 (7)	1.260 (8)	110.8 (4)	2.82	O	(x)
(25a)	1 + 2	—	1.409 (3)	1.275 (4)	110.7 (4)	2.83	O	(y)
(25b)	1 + 2	—	1.413 (3)	1.277 (3)	112.0 (2)	2.77	O	(y)
(26)	1 + 2	D	1.41 (1)	1.29 (1)	112.8 (6)	2.86	O	(z)
(27a)	1 + 2	D	1.408 (5)	1.291 (6)	113.1 (4)	2.79	O	(aa)
(27b)	1 + 2	D	1.413 (5)	1.278 (6)	112.7 (4)	2.81	O	(aa)
(28)	1 + 2	—	1.410 (4)	1.274 (5)	112.4 (2)	2.79	O	(bb)
(29)	1 + 2	Ar	1.408 (3)	1.261 (4)	111.2 (2)	2.85	O	(cc)
(30)	1 + 2	Ar	1.405 (9)	1.26 (1)	109.8 (6)	2.83	O	(dd)
(31)	1 + 2	D/	1.405 (5)	1.278 (5)	113.0 (3)	2.84	O	(ee)
(32)	1 + 2	Ar	1.405 (6)	1.270 (6)	112.9 (4)	2.62	O	(ff)
(33)	1 + 2	Ar	1.405 (4)	1.269 (4)	112.2 (3)	<u>2.65</u>	O	(gg)
(34)	1 + 2	—	1.40 (1)	1.26 (1)	112.2 (8)	2.80	O	(hh)
(35)	1 + 2	D	1.42 (1)	1.31 (1)	109.1 (7)	2.74	O	(ii)
(36)	1 + 2	Ar	1.420 (4)	1.264 (5)	112.1 (3)	2.78	O	(jj)
(37)	1 + 2	Ar/	1.412 (3)	1.270 (3)	113.6 (2)	2.81	O	(kk)
(38a)	1 + 2	Ar/	1.418 (4)	1.278 (4)	113.1 (3)	2.79	O	(ll)
(38b)	1 + 2	Ar/	1.423 (4)	1.279 (4)	111.3 (3)	2.74	O	(ll)
(39)	1 + 2	—	1.430 (2)	1.284 (2)	111.8 (2)	2.78	O	(mm)
(40)	1 + 2	Ar/	1.424 (3)	1.287 (3)	112.1 (2)	2.82	O	(nn)
(41)	1 + 2	—	1.419 (2)	1.280 (3)	113.8 (2)	2.78	O	(oo)
(42)	1 + 2	—	1.425 (1)	1.275 (2)	112.4 (1)	2.81	O	(oo)
(43)	1 + 2 + 3	Ar/	1.422 (3)	1.289 (3)	110.1 (2)	2.79	O	(pp)
(44)	1 + 2 + 3	—	1.420 (2)	1.263 (2)	110.4 (2)	2.83	O	(hh)
(45)	1 + 2 + 3	Ar/	1.438 (7)	1.272 (7)	110.7 (5)	2.73	O	(qq)
(46)	1 + 2 + 3	—	1.435 (4)	1.284 (4)	110.0 (3)	2.73	O	(rr)

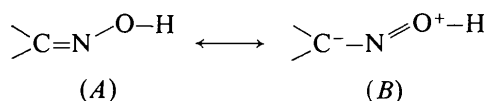
Table 6 (cont.)

References: (a) van Oijen & Romers (1966). (b) Talberg (1974). (c) Martínez-Ripoll & Lorenz (1974). (d) Martínez-Ripoll & Lorenz (1976b). (e) Declercq, Germain & Van Meerssche (1975). (f) Martínez-Ripoll & Lorenz (1976a). (g) Allen *et al.* (1970). (h) Present work (HIB). (i) Present work (HIOP). (j) Martínez-Ripoll & Lorenz (1973). (k) Braibanti *et al.* (1973). (l) Briansó, Miravittles, Plana & Font-Altaba (1973). (m) Jones & Chaney (1972). (n) Briansó, Miravittles, Font-Altaba, Declercq & Germain (1973). (o) Tranqui, Cromer & Boucherle (1974). (p) Jensen & Jerslev (1967). (q) Wetherington & Moncrief (1973). (r) Jensen (1970). (s) Winkler, Seiler, Chesick & Dunitz (1976). (t) Calleri *et al.* (1966). (u) Calleri, Bonaccorti & Viterbo (1977). (v) Plana, Miravittles, Briansó & Font-Altaba (1973). (w) Oonk & Kroon (1976). (x) Følting, Lipscomb & Jerslev (1964). (y) Groth (1968). (z) Calleri, Chawdhury & Viterbo (1976). (aa) Kroon, van Gurp, Oonk, Baert & Fouret (1976). (bb) Kjaer, Larsen & Sivertsen (1977). (cc) Bachechi & Zambonelli (1973). (dd) Brehm & Watson (1972). (ee) Saarinen *et al.* (1977). (ff) Pfluger & Harlow (1973). (gg) Pfluger, Pfluger & Brackett (1978). (hh) Mostad (1978). (ii) Andreetti, Cavalca, Manfredotti & Musatti (1969). (jj) Bachechi & Zambonelli (1972). (kk) Fortier, Birnbaum, Buchanan & Dawson (1980). (ll) Dignam, Hegarty & Begley (1980). (mm) Bright, Plessius & de Boer (1973). (nn) Gozlan, Michelot, Riche & Rips (1977). (oo) Groth (1979). (pp) Dondoni *et al.* (1976). (qq) Gieren & Dederer (1977) (rr) Gozlan & Riche (1976).

than N(2), both in HIB and HIOP, providing a theoretical basis for the experimental evidence of infinite chains of O(1)—H(1)···N(1) hydrogen bonds found in the crystals.

In a few cases, reported at the end of Table 6, the oxime group is observed to form, besides HB's of types 1 and 2, a third HB where the oxygen is a HB acceptor. In two of the four cases observed this is an intramolecular N—H···O bond which closes a five-membered ring in amide oxime derivatives and therefore displays a bond angle at the H atom far from 180°. For this reason there are some doubts that it can be a true HB and alternative interpretations based on Epiotis's nonbonded attractive  $p\pi$  or  $p\sigma$  interactions have been suggested (Dondoni, Gilli & Sacerdoti, 1976, and references therein).

Both distances and angles of the oxime group show a remarkable degree of variability but their variations are practically uncorrelated, as shown by the values of the correlation coefficients,  $r$ . In fact,  $r(\text{N—O}/\text{C=N—O})$  on the full set is  $-0.43$  and  $r(\text{N—O}/\text{C=N})$  is  $-0.42$  only if samples (35) and (19f) of Table 6 are omitted, otherwise it is as small as  $-0.28$ . The most striking feature is the rather wide interval (1.36–1.44 Å) in which the N—O distances are observed to fall, an interval which, in comparison with the C—C bond distances, is found to correspond to a variation of Pauling's bond number greater than 0.5. Such an effect is usually interpreted in terms of VB theory as the result of different contributions of the polar form (B) to the ground state of the molecule,



according to the different nature of the substituents and, above all, to the ability of the molecule to transmit the negative charge through a conjugated double-bond system. Loosely speaking, this hypothesis is confirmed by the data of Table 6, as the shortest N—O distances are associated with molecules having extended conjugated systems (marked DD in the table) while the

longest ones with molecules not having a possibility of conjugation, either for lack of additional  $\pi$  bonds or as a consequence of decoupling caused by rotation (marked by a dash or a slash, respectively, in the table). However, there are several distances which do not comply with this scheme and, moreover, the proposed VB model implies an intercorrelation between N—O and C=N distances which is not observed in practice, so that it may be concluded that experimental errors are most likely larger than the expected structural effects.

A point of possible interest is that N—O distances appear to depend on the number and type of HB's formed by the oxime group in the crystals. This is illustrated in Fig. 9. All the oxime groups of Table 6 were divided into three classes according to the number of HB's formed; that is, HB's of types 1, 1 + 2 and 1 + 2 + 3 are formed by members of classes A, B and C respectively. The total distribution of the N—O distances has a mean of 1.408 Å with a standard deviation of 0.002 Å and the values appear to be nearly normally distributed.\* However, if the N—O distances

\* Mean values ( $X_m$ ) and their standard errors ( $\sigma_m$ ) have been calculated from the individual values ( $x_i$ ;  $\sigma_i$ ) according to the formula  $X_m = \sum_i (x_i/\sigma_i^2) / \sum_i (1/\sigma_i^2)$ ;  $\sigma_m = \{ \sum_i [(x_i - X_m)^2/\sigma_i^2] / (N - 1) \sum_i (1/\sigma_i^2) \}^{1/2}$ .

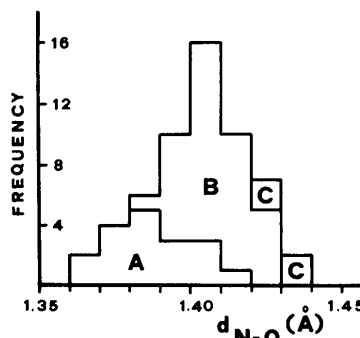


Fig. 9. Distribution of N—O distances (Å) in oximes of known molecular structure. Areas marked A, B, C are the sub-distributions of N—O distances for samples belonging to the three classes defined in the text.



belonging to members of the three classes are grouped together they are found not to be randomly distributed but to give rise to three partially overlapping sub-distributions with means  $1.388 \pm 0.003$ ,  $1.416 \pm 0.002$  and  $1.425 \pm 0.004$  Å for the three classes *A*, *B* and *C* respectively. This result must be regarded with caution owing to the practical difficulty of knowing whether, or in which way, small samples casually drawn from an almost infinite population of molecules may be biased; this notwithstanding it appears to be indicative of a definite dependence of the N—O distance on the number of HB's accepted by the oxime group. This hypothesis would not be unrealistic from a physical point of view, as the charge transfer from the oxime N (HB type 2) could reduce the electron density in the region between the two atoms, with a consequent weakening of the N—O bond, and that from the oxime O (HB type 3) would decrease the contribution of the polar form *B* to the ground state of the molecule.

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## Dihydroelephantopin, C<sub>19</sub>H<sub>22</sub>O<sub>7</sub>

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### Abstract

C<sub>19</sub>H<sub>22</sub>O<sub>7</sub>,  $M_r = 362.38$ , is orthorhombic,  $P2_12_12_1$ , with  $a = 10.952(4)$ ,  $b = 25.642(19)$ ,  $c = 6.386(2)$  Å,  $V = 1793(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_c = 1.342$  Mg m<sup>-3</sup>,  $\mu = 0.87$  mm<sup>-1</sup>. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1568 reflexions led to a final  $R$  of 0.061. Dihydroelephantopin is a germacranolide-type sesquiterpene lactone containing a ten-membered ring which exhibits a chair–chair conformation in the solid state. The C(4)–C(5) double bond of the germacradiene skeleton has been transformed into a *trans* epoxide function. The C(15) methyl group has been oxidized and forms an  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone by closure at C(2) with the C(1)–C(10) double bond remaining undisturbed. The second  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone is *trans*-fused at C(6)–C(7) and exhibits an exocyclic double bond. Dihydroelephantopin exhibits antitumor activity.

### Introduction

The genus *Elephantopus* (Compositae) is a member of the tribe Vernonieae, and is composed of approximately 32 species which are distributed throughout the tropical areas of the world (Heywood, Harborne & Turner, 1977). Perhaps a dozen of these species are found in the United States with *Elephantopus*

*tomentosus* distributed from Eastern Texas through the Southeastern portions of the country. *E. mollis*, *E. spicatus* and *E. scaber* have been used as folk remedies in Latin America, India and China to treat wounds and dysentery and as a cardiac tonic, astringent and febrifuge (Altschul, 1973; Nadkarni, Nadkarni & Chopra, 1976). The chemistry of the genus *Elephantopus* is not well enough established to clarify its phyletic position within the tribe Vernonieae; therefore, a survey of the chemistry of members of the genera composing this tribe has been initiated. The sesquiterpene dilactones elephantopin, elephantin and elephantol were isolated from *E. elatus* (Kupchan, Aynehchi, Cassady, McPhail, Sim, Schnoes & Burlingame, 1966; Kupchan, Aynehchi, Cassady, Schnoes & Burlingame, 1969), while deoxyelephantopin and isodeoxyelephantopin were isolated from *E. scaber* L. (Kurkawa, Nakanishi, Wu, Hsu, Maruyama & Kupchan, 1970; Govindachari, Viswanathan & Fuhrer, 1972). The sesquiterpene lactone molephantin was isolated from *E. mollis* (Lee, Furukawa, Kozuka, Huang, Luhan & McPhail, 1973). All compounds exhibit antitumor properties. *Elephantopus tomentosus* L. (tobacco-weed, devil's grandmother) was collected in Georgia and extracted by the usual procedures to yield dihydroelephantopin, a white crystalline compound which exhibits tumor-inhibiting properties against leukemia tumor cells (type PS) (Rustaiyan, Niknejad, Watson, Zabel, Mabry, Yabuta & Jones, 1978). We would like to report the structure of dihydroelephantopin (1).

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