which is farthest from the nitrogen atom, is also the bromide ion closest to the phosphorus atom |4·580 (1) Å|. The ΔF map does not show any indication of a hydrogen atom in the region between this bromide ion and the phosphorus atom. This bromide ion is 'face' oriented with respect to the tetrahedral phosphonium center. This phosphorus to bromide ion arrangement is not significantly different from those of phosphorus to halide ions in other triphenylphosphonium structures (Archer et al., 1981). Each bromide-ion pair also interacts with another nitrogen atom from a symmetry-related molecule, thus forming a network in the crystal which disperses and neutralizes the charges. The region occupied by this network is a channel parallel to the crystallographic a axis (Fig. 2). The charged atoms avoid the phenyl rings as expected (Archer et al., 1981).

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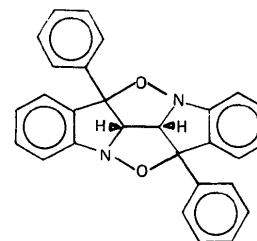# Structure of 1,3′:1′,3-Diepoxy-3,3′-diphenyl-2,2′-biindolinyl

BY JOHN IBALL,* W. D. SAMUEL MOTHERWELL AND IN PART JOHN C. BARNES AND WIGEN GOLNAZARIANS

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Abstract. $C_{28}H_{20}N_2O_2$, $M_r = 416\cdot48$, monoclinic, $C2/c$, $a = 23\cdot85$ (1), $b = 7\cdot90$ (1), $c = 13\cdot07$ (1) Å, $\beta = 120\cdot4$ (2)°, $V = 2124\cdot0$ Å^3, $Z = 4$, $D_x = 1\cdot303$, $D_m = 1\cdot309$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0\cdot58$ mm^{-1}, $F(000) = 872$, $T = 293$ K, $R = 0\cdot056$ for 1751 unique observed reflexions. The molecule contains four five-membered rings fused into a dome. The O atoms lie out of plane of their rings to maximize the $O(1)\cdots O(1')$ distance. The phenyl groups are placed to minimize steric effects. The principal motion of the phenyl groups is a wag about the points of attachment to the molecule, C(13) and C(13').

Introduction. The title compound (I) was crystallized in ca 8% yield from the reaction of phenylacetylene and nitrosobenzene. The chemical properties and a partially

refined crystal structure (R 0·13) have been reported previously (Iball, Motherwell, Pollock & Tedder, 1968). The model has now been refined to convergence using the original data set.

(I)

Experimental. The colourless compound crystallizes in well formed diamond-shape prisms and the samples

used for X-ray data collection were grown from chloroform solution. Density measured using a density column containing aqueous $KI/Na_2S_2O_3$. Unit cell obtained from X-ray photographs and refined from diffractometer measurements on 12 reflexions. Data collected on a Wooster four-circle diffractometer using fixed χ mode, $\theta \leq 75°$ (Cu $K\alpha$) for a crystal (0·25 × 0·4 × 0·3 mm) accurately mounted on the b axis, for range $-30 \leq h \leq 26$, $0 < k < 9$, $0 < l < 16$. 2269 unique reflexions measured of which 1751 with $|F_o| > 3·0$ used in refinement. No variation in intensity with time observed. No correction for absorption.

All calculations in present refinement performed on the Dundee University DEC 10 computer, *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO*78 (Motherwell & Clegg, 1978); atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Structure solved by manual symbolic addition (Karle & Karle, 1966) using all $|E| > 1·50$. Signs determined for 231 reflexions. E map showed all non-H atoms with no background peak above 0·5 times the weakest C atom. An unpublished refinement using local programs converged at $R = 0·063$ with all non-H atoms having anisotropic thermal parameters. These coordinates were used to start the present refinement which converged at $R = 0·056$ with anisotropic thermal parameters for all non-H atoms. H atoms placed on calculated positions with refined grouped isotropic thermal parameters except for H(14) which was located on a difference synthesis and refined.

Final refinement: minimizing $\sum w(|F_o| - |F_c|)^2$, 152 refined parameters, $wR = 0·0847$, $w = 1·00/[\sigma(F) + 0·004725(F)^2]$, $(\Delta/\sigma)_{av} = 0·013$, $(\Delta/\sigma)_{max} = 0·088$ [U_{22} of C(14)], max. diff. peak 0·18 e Å^{-3}, max. negative diff. electron density $-0·21$ e Å^{-3}.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* The dimeric molecule (Fig. 1) is located with a molecular twofold axis coincident with a space-group twofold axis, and contains a novel arrangement of four fused five-membered rings in a dome-shaped configuration. The bond lengths and angles (Table 2) are of the expected magnitude, and the intermolecular contacts do not include any abnormal values.

Analysis of the mean planes of the rings as labelled in Fig. 1 shows that plane B is close to coplanar with plane A [dihedral angle 4·4 (2)°].† The r.m.s. deviation

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and inter-ring angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42563 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† A table listing inter-ring angles has been deposited. See deposition footnote.

Table 1. *Coordinates* ($\times 10^4$) *for non-H atoms and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	634 (1)	1236 (3)	3852 (2)	41 (1)
C(2)	679 (1)	−207 (3)	4495 (2)	51 (1)
C(3)	970 (1)	−1618 (3)	4336 (2)	56 (1)
C(4)	1214 (1)	−1592 (3)	3573 (2)	57 (1)
C(5)	1159 (1)	−145 (3)	2920 (2)	50 (1)
C(6)	862 (1)	1269 (3)	3062 (2)	42 (1)
C(7)	1290 (1)	3904 (3)	2531 (2)	43 (1)
C(8)	1896 (1)	3777 (3)	3558 (2)	55 (1)
C(9)	2418 (1)	4727 (4)	3699 (3)	65 (1)
C(10)	2345 (1)	5798 (4)	2808 (3)	66 (1)
C(11)	1747 (1)	5930 (4)	1780 (3)	64 (1)
C(12)	1219 (1)	4997 (3)	1643 (2)	53 (1)
C(13)	714 (1)	2955 (3)	2437 (2)	42 (1)
C(14)	357 (1)	3908 (3)	2983 (2)	41 (1)
O(1)	−234 (1)	2801 (2)	3821 (1)	46 (1)
N(1)	407 (1)	2853 (2)	3964 (2)	43 (1)

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(2)–C(1)	1·388 (3)		C(9)–C(8)	1·385 (3)
C(6)–C(1)	1·390 (3)		C(10)–C(9)	1·377 (4)
N(1)–C(1)	1·423 (3)		C(11)–C(10)	1·382 (4)
C(3)–C(2)	1·382 (4)		C(12)–C(11)	1·390 (3)
C(4)–C(3)	1·386 (4)		C(14)–C(13)	1·553 (3)
C(5)–C(4)	1·392 (3)		N(1)–C(14)	1·482 (3)
C(6)–C(5)	1·384 (3)		N(1)–O(1)	1·445 (2)
C(13)–C(6)	1·508 (3)		C(14)–C(14')	1·524 (4)
C(8)–C(7)	1·391 (3)		C(1)⋯C(6')	3·156 (3)
C(12)–C(7)	1·386 (3)		O(1)⋯O(1')	4·396 (4)
C(13)–C(7)	1·515 (3)			

C(6)–C(1)–C(2)	121·8 (2)		C(10)–C(9)–C(8)	120·0 (2)
N(1)–C(1)–C(2)	126·2 (2)		C(11)–C(10)–C(9)	119·7 (2)
N(1)–C(1)–C(6)	111·8 (2)		C(12)–C(11)–C(10)	120·5 (2)
C(3)–C(2)–C(1)	117·4 (2)		C(11)–C(12)–C(7)	120·2 (2)
C(4)–C(3)–C(2)	121·5 (2)		C(7)–C(13)–C(6)	116·0 (2)
C(5)–C(4)–C(3)	120·6 (2)		C(13)–C(14)–C(14')	104·9 (3)
C(6)–C(5)–C(4)	118·4 (2)		N(1)–C(14)–C(14')	106·4 (3)
C(5)–C(6)–C(1)	120·2 (2)		N(1')–O(1)–C(13)	108·2 (3)
C(13)–C(6)–C(1)	110·3 (2)		C(14)–C(13)–C(6)	102·2 (2)
C(13)–C(6)–C(5)	129·5 (2)		C(14)–C(13)–C(7)	114·1 (2)
C(12)–C(7)–C(8)	118·7 (2)		N(1)–C(14)–C(13)	107·6 (2)
C(13)–C(7)–C(8)	119·8 (2)		C(14)–N(1)–C(1)	106·5 (2)
C(13)–C(7)–C(12)	121·2 (2)		O(1')–N(1)–C(1)	113·2 (2)
C(9)–C(8)–C(7)	120·9 (2)		O(1')–N(1)–C(14)	106·8 (1)

(') denotes equivalent position $-x, y, \tfrac{1}{2} - z$.
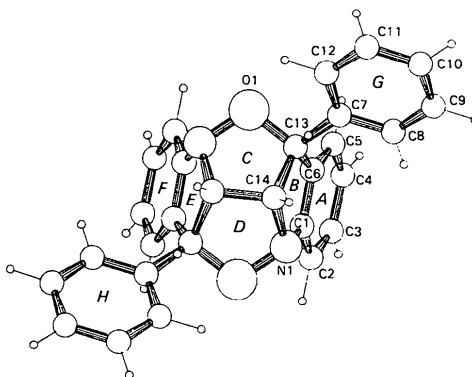

Fig. 1. Molecule viewed down **b**, showing numbering scheme for atoms. Letters $A–H$ identify the ring planes cited in the text and in the deposited table of dihedral angles.

of an atom from plane B is 0·052 (3) Å, compared with 0·005 (5) Å for plane A. In ring C O(1) lies 0·396 (2) Å above the mean plane of the other four atoms [r.m.s. deviation for plane C' 0·027 (3) Å]. This configuration maximizes the O(1)···O(1') distance [4·396 (4) Å] at the expense of reducing C(1)···C(6') to 3·156 (3) Å. Studies of a model show that the molecule is potentially very flexible. There is only a small energy barrier between the observed position and the configuration with O(1) about 0·4 Å below the plane C', for which O(1)···O(1') would be 3·2 Å and C(1)···C(6') 4·6 Å. However, the thermal ellipsoid of O(1) is small and shows no sign that this 'breathing' vibration of the molecule is important in the crystal. It appears that the observed configuration minimizes the effective molecular volume and gives the lowest packing energy, in spite of the short C(1)···C(6') distance.

The phenyl group F adopts a position of minimum steric interaction, with the torsion angle C(8)—C(7)—C(13)—C(14) 84·9 (3)°. Examination of the thermal ellipsoids of the ring shows that the main motion is a wagging about C(13) normal to the plane of the ring and not a rotation about C(13)—C(7). Fig. 2 shows the results of packing potential-energy calculations, using OPEC (Gavezzotti, 1983) for these two motions. There is very little energy change involved in either motion over the angular range of ca 2° which would correspond to thermal motion in the crystal. Over a larger angular range the rotation involves a change of only 8·4 kJ mol⁻¹ out to 20° whereas the wagging motion involves the loss of almost two thirds of the packing energy. As a scale for these calculations oscillation of the whole molecule about C(14)—C(14') was also considered. The energy profile is very much steeper than for either of the motions possible for the phenyl groups.
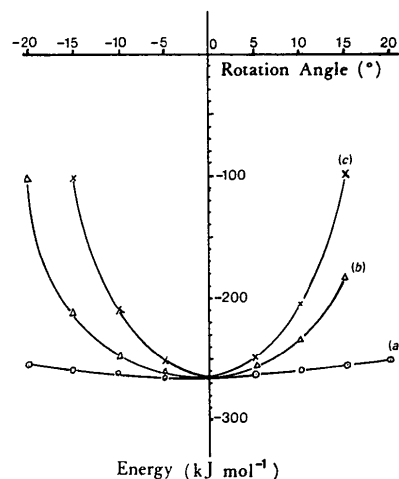

Fig. 2. Packing potential energy as a function of rotation. (a) Rotation of the phenyl group G about the C(7)—C(13) bond. The remainder of the molecule and all adjacent molecules at rest. (b) Wagging of the phenyl group G about C(13) as pivot and normal to rest position of the ring. The remainder of the molecule and all adjacent molecules at rest. (c) Rotation of the whole molecule about C(14)—C(14'), adjacent molecules at rest.

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Structure of a Benzofuranone Oxime

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Abstract. (1R,2S,3R,4S,3'R)-1-(2,3,4,5,6,7-Hexahydro-2-hydroxyimino-4-oxo-3-benzo[b]furyl)-1,2,3,4,5-pentanepentayl pentaacetate, $C_{23}H_{29}NO_{13}$, $M_r = 527·5$, orthorhombic, $P2_12_12_1$, $a = 10·669$ (1), $b = 28·112$ (2), $c = 8·432$ (1) Å, $V = 2529·0$ (4) Å³, $Z = 4$, $D_m = 1·37$, $D_x = 1·38$ Mg m⁻³, $\lambda(Mo K\alpha) = 0·71069$ Å, $\mu = 0·107$ mm⁻¹, $F(000) = 1112$, $T = 300$ K, final $R = 0·073$ for 2525 observed $[I \geq 2\sigma(I)]$ independent reflections. The form of the oxime is Z. The cyclohexene ring conformation is intermediate between half-boat and half-chair and the dihedral angle between the planar part of the cyclohexene ring and the furan plane is 5·8 (3)°. There is some electron delocalization along the resonance system O=C—C=C—C of the