Crystal and Molecular Structure of 6,7-Diphenyldibenzo[*e,g*][1,4]diazocine, a Heterocyclic Cyclo-octatetraene [1]

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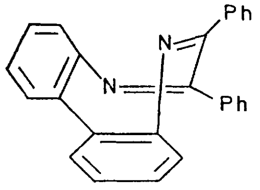
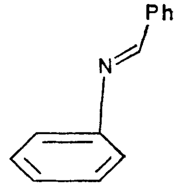
The crystal and molecular structure of the title compound has been determined by direct methods from 1581 non-zero reflections measured diffractometrically. Crystals are orthorhombic, space group *Pbcn*, with a = 14·798(2), b = 10·355(1), and c = 11·992(2) Å, Z = 4 and the molecule occupies the two-fold axis of the space group. Least-squares refinement gave a final R of 0·037. Bond lengths for C–N of 1·424(2) and 1·274(2) Å were determined for bonds of nearly single- and double-bond character.

THE resolution of the 3,10-dicarboxylic acid derivative of the title compound by Bell[2] in 1952 proved that the molecule must exist in the tub conformation accepted for cyclo-octatetraene (COT). The tub form has been previously shown to exist by X-ray diffraction and electron diffraction of COT and some of its methyl derivatives.[3] In 1963 an attempt was made[4] to racemize Bell's compound thermally. Thermal elimination to benzonitrile and 9-phenylphenanthridine-2,7-dicarboxylic acid thwarted the attempted racemization but set a minimum activation energy for racemization at >48 kcal mol^{-1}.

6,7-Diphenyldibenzo[*e,g*][1,4]diazocine (I) contains C_{sp^2}–N_{sp^2} linkages which are formally single and double bonds, and which should differ significantly in length from the C–N bond in pyridine. There is a paucity of data on the bond lengths of these types of bonds. Burgi and Dunitz[5] reported the solution of the structure of benzylideneaniline (II), but experimental difficulties (*vide infra*) prevented a precise structure determination.



(I)



(II)

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[1] Presented at the Amer. Cryst. Assn. Meeting, Gainesville, Florida, January, 1973, Paper *E*10.

[2] F. Bell, *J. Chem. Soc.*, 1952, 1527.

[3] G. Avitabile, P. Ganis, and V. Petraccone, *J. Phys. Chem.*, 1969, **73**, 2378; J. Bordner, R. G. Parker, and R. H. Stanford, jun., *Acta Cryst.*, 1972, **B28**, 1069.

[4] N. L. Allinger, W. Szkrybalo, and M. A. DaRooge, *J. Org. Chem.*, 1963, **28**, 3007.

[5] H. B. Burgi and J. D. Dunitz, *Helv. Chem. Acta*, 1970, **53**, 1747.

Meunier-Piret *et al.*[6] reported the structure of 4′-methoxy-4-nitro-*N*-benzylideneaniline but they also encountered difficulties. We required accurate data on such bonds for parameterization of some molecular mechanics work on nitrogen heterocycles, which we have already carried out on other classes of compounds.[7] We therefore decided to undertake an *X*-ray structure determination of (I).

EXPERIMENTAL

Compound (I) was recrystallized from acetic acid. A suitable needle crystal was cut along the needle axis to $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}6$ mm and mounted along the long (*c*) axis of the needle. Initial crystal data were obtained on a precession camera, and initial cell-dimensions were calculated. The molecule is required to occupy the two-fold axis of the space group.

Crystal Data.—$C_{26}H_{18}N_2$, $M = 358{\cdot}44$. Orthorhombic, $a = 14{\cdot}798(2)$, $b = 10{\cdot}355(1)$, $c = 11{\cdot}992(2)$ Å, $U = 1836{\cdot}6$ Å^3, $D_m = 1{\cdot}289$ (by flotation in cyclohexane–carbon tetrachloride), $Z = 4$, $D_c = 1{\cdot}295$, $F(000) = 992$. Space group, *Pbcn*, from systematic absences.[8] Cu-$K_{\bar{\alpha}}$ radiation (for intensity measurement), $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_{\bar{\alpha}}) = 5{\cdot}98$ cm^{-1}.

Structure Determination.—Data were collected on an Enraf–Nonius CAD 4 diffractometer by use of the ω—2θ scan with Cu$K_{\bar{\alpha}}$ radiation and a graphite monochrometer. Least-squares refinement of 15 accurately centered reflections gave the cell dimensions. A total of 3633 points in two equivalent octants were collected with $\sin\theta/\lambda < 0{\cdot}619$ out of a possible 4250 for a quadrant.[9] Data were corrected for Lorentz and polarization effects but not for absorption.[10] After elimination of all points with $I < 2\sigma$ * above background and averaging equicalent points,[10] † 1581 unique non-zero reflections were available for use in the analysis. Examination of a series of three standard reflections, taken after every 51st reflection, indicated that no significant decomposition of the crystal had occurred during data collection.

Solution and Refinement of Structure.—The data were placed on an absolute scale [12] and *E* values obtained by use of FAME.[13] An attempt to phase *E* values $> 1{\cdot}5$ by use of MAGIC, LINK, and SYMPL failed because a complete origin-set could not be determined. The 194 points with $E > 1{\cdot}50$ were used as input to MULTAN.[14] One of the sets of phases produced by MULTAN had all 194 points phased with weights $>95\%$ and had an absolute figure of merit $>1{\cdot}40$. When these phased data were used to generate an *E* map, initial positions for all non-hydrogen atoms were obtained; a structure-factor calculation using these coordinates gave an initial *R* of 39·5%. These positions and isotropic temperature factors were refined with unit weights and then anisotropically using weights of $1/\sigma(F_{hkl})$.[15] *R* was then 9·5%. A difference-Fourier map generated from data from the least-squares refinement revealed all 9 unique hydrogen atom positions. At this point, refinement with weights of $1/\sigma(F_{hkl})$, treating all hydrogens isotropically, and all non-hydrogens anisotropically using the average *F* values (*vide supra*) gave a final *R* of 3·7%. A difference map utilizing data from the final refinement showed no peak with electron density $>0{\cdot}25$ eÅ^{-3}.

RESULTS AND DISCUSSION

Data relative to (I), with the crystallographic numbering of Figure 1, are given in Tables 1—4. Table 1 gives the final atomic position and thermal parameters with the bond lengths and bond angles given in Tables 2 and 3; σ for calculated values are given in parentheses in each Table. Bond lengths and angles are provided only for the unique half of the molecule. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20776 (12 pp., 1 microfiche; see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, index issue).

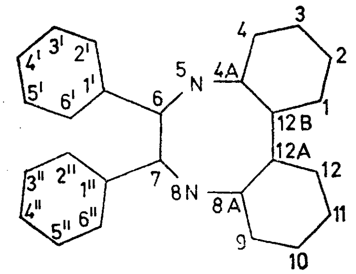

FIGURE 1 The molecule of (I) showing the crystallographic numbering used in this analysis

Burgi and Dunitz [5] report 1·460(3) and 1·237(3) Å for the two C–N bond lengths and 119·9(3)° for the C–N–C bond angle in (II). These data appear to be

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* $\sigma(F_{hkl})$ is obtained from counting statistics [11] and is computed by: $\sigma(F_{hkl}) = \{(at + 1)I + 4(B_l + B_r) + (\kappa I_r)^2/s[I - 2(B_l + B_r)]\}^{\frac{1}{2}}/2\sqrt{Lp}$, where I = total measured peak intensity + backgrounds, B_l = left background, B_r = right background, $I_r = \{(at + 1)/s\}I - 2(B_l + B_r)$, s = scan speed, l = attenuation filter ($t = 1$ if filter used, $t = 0$ if no filter), a = attenuation filter factor (23·5), κ = standard deviation for instrumental instability (determined from control reflections), and Lp = Lorentz-polarization correction.

† The structure was initially solved by using only one of the equivalent points with the better sigma giving *R* 5·7%. Later, we decided to average equivalent *F* values in the final least-squares. The σ for F_{avg} was calculated by $\sigma_{avg} = [(\sigma_1{}^2 + \sigma_2{}^2)/4]^{\frac{1}{2}}$. *R* was reduced by 0·1% from the original, and the estimated standard deviations of positions improved an average of only 1 in the last significant figure. This is not surprising since the equivalent points had very nearly identical *F* values. The averaged data are those reported.

[6] J. Meunier-Piret, P. Piret, G. Germain, and M. Van Meerssche, *Bull. Soc. chim. belges*, 1972, **81**, 533.

[7] N. L. Allinger and J. Sprague, *J. Amer. Chem. Soc.*, 1973, **95**, 3893, and earlier papers.

[8] G. H. Stout and L. H. Jenzen, '*X*-ray Structure Determination, A Practical Guide,' Macmillan, New York, 1968, p. 134.

[9] See ref. 8, p. 34.

[10] DATRED, by C. J. Finder and M. G. Newton, University of Georgia, Athens, Georgia, 1972.

[11] See ref. 8, pp. 454—458.

[12] A. J. C. Wilson, *Nature*, 1942, **150**, 152,

[13] FAME, MAGIC, LINK, and SYMPL, a series of direct-phasing computer programs by R. A. Dewar, A. Stone, and E. B. Fleischer, University of Chicago, Chicago.

[14] MULTAN, a computer program for the automatic solution of crystal structure by P. Main and M. M. Woolfson, University of York, York, and G. Germain, University of Louvain, Leuven, Belgium.

[15] UCLALS, P. K. Gantzel, R. K. Sparks, K. N. Trueblood, University of California at Los Angeles; modified by M. G. Newton for the IBM 360.

TABLE 1

Final atomic positions and temperature factors

Atom	x	y	z	$B_{iso} \times 10^2$ or $\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^5$
C(12B)	0·47677(08)	0·11908(11)	0·30496(11)	332(06)	598(11)	510(10)	68(12)	−35(12)	104(16)
C1	0·42036(10)	0·01615(13)	0·33422(13)	436(07)	632(12)	654(12)	−87(15)	37(15)	79(19)
C(2)	0·37629(11)	0·01328(14)	0·43582(14)	466(08)	779(13)	736(12)	−157(18)	129(16)	317(21)
C(3)	0·38862(11)	0·11210(14)	0·51132(13)	464(08)	984(15)	577(12)	24(17)	164(16)	284(22)
C(4)	0·44692(10)	0·21299(13)	0·48642(12)	427(07)	815(13)	497(10)	12(15)	−8(14)	22(19)
C(4A)	0·49019(08)	0·21765(11)	0·38340(10)	316(06)	631(11)	475(10)	29(13)	−92(12)	124(16)
N(5)	0·55504(07)	0·31708(10)	0·36513(09)	326(05)	640(10)	498(08)	0(11)	−97(10)	22(14)
C(6)	0·54220(08)	0·39678(11)	0·28572(10)	264(05)	559(10)	483(09)	57(12)	−73(12)	−120(15)
C(1′)	0·60861(08)	0·50059(11)	0·26158(11)	257(05)	545(10)	536(09)	55(13)	−53(12)	−76(16)
C(2′)	0·60622(09)	0·56466(13)	0·15978(12)	357(07)	711(12)	614(11)	−87(14)	−170(14)	131(19)
C(3′)	0·66637(10)	0·66426(14)	0·13718(14)	435(08)	792(14)	756(13)	−170(17)	−26(16)	313(22)
C(4′)	0·72859(10)	0·70078(14)	0·21647(14)	379(07)	783(13)	905(14)	−294(16)	32(16)	0(22)
C(5′)	0·73224(10)	0·63707(15)	0·31762(14)	361(07)	990(15)	785(13)	−293(16)	−171(16)	−237(23)
C(6′)	0·67298(09)	0·53700(13)	0·34044(13)	333(06)	843(14)	590(11)	−97(14)	−122(14)	−58(19)
C(1)H	0·4103(10)	−0·0558(13)	0·2777(13)	150(31)					
C(2)H	0·3322(11)	−0·0606(14)	0·4545(13)	204(34)					
C(3)H	0·3567(11)	0·1102(15)	0·5846(14)	215(35)					
C(4)H	0·4589(09)	0·2816(12)	0·5438(12)	110(29)					
C(2′)H	0·5623(11)	0·5379(14)	0·1006(14)	185(33)					
C(3′)H	0·6628(11)	0·7068(16)	0·0616(15)	248(37)					
C(4′)H	0·7720(12)	0·7697(17)	0·1995(15)	300(39)					
C(5′)H	0·7783(12)	0·6644(16)	0·3722(14)	288(39)					
C(6′)H	0·6747(10)	0·4917(15)	0·4133(14)	172(32)					

TABLE 2

Bond lengths (Å)

(*a*) Heavy-atom bonds

C(12A)–C(12B)	1·486(2)	C(6)–C(7)	1·515(2)
C(12B)–C(4A)	1·402(2)	C(6)–C(1′)	1·485(2)
C(12B)–C(1)	1·398(2)	C(1′)–C(2′)	1·390(2)
C(1)–C(2)	1·382(2)	C(1′)–C(6′)	1·394(2)
C(2)–C(3)	1·378(2)	C(2′)–C(3′)	1·389(2)
C(3)–C(4)	1·387(2)	C(3′)–C(4′)	1·376(2)
C(4)–C(4A)	1·392(2)	C(4′)–C(5′)	1·381(2)
C(4A)–N(5)	1·424(2)	C(5′)–C(6′)	1·384(2)
N(5)–C(6)	1·274(2)		

(*b*) Bonds to hydrogen

C(1)–C(1)H	1·02(1)	C(2′)–C(2′)H	1·00(2)
C(2)–C(2)H	1·03(2)	C(3′)–C(3′)H	1·01(2)
C(3)–C(3)H	1·00(2)	C(4′)–C(4′)H	0·98(2)
C(4)–C(4)H	1·00(1)	C(5′)–C(5′)H	0·99(2)
C(6′)–C(6′)H	0·99(2)		

TABLE 3

Angles (deg.)

C(1)–C(12B)–C(4A)	118·1(1)	N(5)–C(6)–C(7)	123·1(1)
C(1)–C(12B)–C(12A)	119·9(1)	C(1′)–C(6)–C(7)	115·8(1)
C(4A)–C(12B)–C(12A)	122·0(1)	C(6)–C(1′)–C(2′)	120·0(1)
C(12B)–C(1)–C(2)	121·3(1)	C(6)–C(1′)–C(6′)	121·0(1)
C(12B)–C(1)–C(1H)	118·5(08)	C(2′)–C(1′)–C(6′)	119·0(1)
C(2)–C(1)–C(1H)	120·1(08)	C(1′)–C(2′)–C(3′)	120·6(1)
C(1)–C(2)–C(3)	120·0(1)	C(1′)–C(2′)–C(2′)H	120·5(09)
C(1)–C(2)–C(2)H	120·4(09)	C(3′)–C(2′)–C(2′)H	118·9(09)
C(3)–C(2)–C(2)H	119·5(09)	C(2′)–C(3′)–C(4′)	119·9(1)
C(2)–C(3)–C(4)	120·0(1)	C(2′)–C(3′)–C(3′)H	117·8(09)
C(2)–C(3)–C(3)H	120·1(09)	C(4′)–C(3′)–C(3′)H	122·4(09)
C(4)–C(3)–C(3)H	119·9(09)	C(3′)–C(4′)–C(5′)	120·1(1)
C(3)–C(4)–C(4A)	120·2(1)	C(3′)–C(4′)–C(4′)H	119·6(10)
C(3)–C(4)–C(4)H	119·6(08)	C(5′)–C(4′)–C(4′)H	120·2(10)
C(4A)–C(4)–C(4H)	120·1(08)	C(4′)–C(5′)–C(6′)	120·4(1)
C(12B)–C(4A)–C(4)	120·3(1)	C(4′)–C(5′)–C(5′)H	118·2(10)
C(12B)–C(4A)–N(5)	121·2(1)	C(6′)–C(5′)–C(5′)H	121·4(10)
C(4)–C(4A)–N(5)	118·1(1)	C(1′)–C(6′)–C(5′)	120·1(1)
C(4A)–N(5)–C(6)	118·8(1)	C(1′)–C(6′)–C(6′)H	119·2(09)
N(5)–C(6)–C(1′)	121·0(1)	C(5′)–C(6′)–C(6′)H	120·7(09)

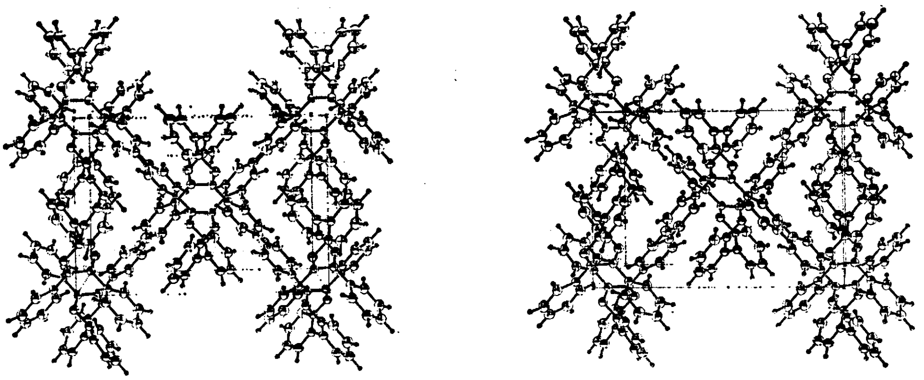

FIGURE 2 A stereodiagram of the unit-cell packing of (I) viewed down *c*. The vertical axis is *b*

TABLE 4

Dihedral angles (deg.) *

C(4A)–C(12B)–C(1)–C(2)	2·3(2)
C(4A)–C(12B)–C(1)–C(1)H	−179·9(08)
C(12A)–C(12B)–C(1)–C(2)	−179·9(1)
C(12A)–C(12B)–C(1)–C(1)H	2·3(10)
C(1)–C(12B)–C(4A)–C(4)	−1·1(2)
C(1)–C(12B)–C(4A)–N(5)	172·2(1)
C(12A)–C(12B)–C(4A)–C(4)	178·7(1)
C(12A)–C(12B)–C(4A)–N(5)	−5·4(2)
C(1)–C(12B)–C(12A)–C(12)	−57·0(2)
C(1)–C(12B)–C(12A)–C(8A)	120·6(1)
C(4A)–C(12B)–C(12A)–C(12)	120·6(1)
C(4A)–C(12B)–C(12A)–C(8A)	−61·8(2)
C(12B)–C(1)–C(2)–C(3)	1·0(2)
C(12B)–C(1)–C(2)–C(2H)	176·6(10)
C(1H)–C(1)–C(2)–C(3)	−178·7(10)
C(1H)–C(1)–C(2)–C(2)H	1·1(14)
C(1)–C(2)–C(3)–C(4)	−1·5(2)
C(1)–C(2)–C(3)–C(3)H	179·8(10)
C(2)H–C(2)–C(3)–C(4)	179·2(10)
C(2)H–C(2)–C(3)–C(3)H	2·1(15)
C(2)–C(3)–C(4)–C(4A)	−2·7(2)
C(2)–C(3)–C(4)–C(4)H	175·9(09)
C(3)H–C(3)–C(4)–C(4A)	178·6(10)
C(3)H–C(3)–C(4)–C(4)H	−2·8(14)
C(3)–C(4)–C(4A)–C(12B)	−1·4(2)
C(3)–C(4)–C(4A)–N(5)	174·9(1)
C(4)H–C(4)–C(4A)–C(12B)	177·2(09)
C(4)H–C(4)–C(4A)–N(5)	−3·7(09)
C(12B)–C(4A)–N(5)–C(6)	66·3(2)
C(4)–C(4A)–N(5)–C(6)	−120·3(1)
C(4A)–N(5)–C(6)–C(1′)	−178·7(1)
C(4A)–N(5)–C(6)–C(7)	4·2(3)
N(5)–C(6)–C(1′)–C(2′)	163·5(1)
N(5)–C(6)–C(1′)–C(6′)	−17·6(2)
C(5)–C(6)–C(1′)–C(2′)	−19·4(2)
C(7)–C(6)–C(1′)–C(6′)	159·5(1)
N(5)–C(6)–C(7)–N(8)	−78·8(2)
N(5)–C(6)–C(7)–C(1″)	104·1(1)
C(1′)–C(6)–C(7)–N(8)	104·1(1)
C(1′)–C(6)–C(7)–C(1″)	73·0(1)
C(6)–C(1′)–C(2′)–C(3′)	178·3(1)
C(6)–C(1′)–C(2′)–C(2′)H	−3·6(10)
C(6′)–C(1′)–C(2′)–C(3′)	0·6(2)
C(6′)–C(1′)–C(2′)–C(2′)H	177·5(10)
C(6)–C(1′)–C(6′)–C(5′)	177·8(1)
C(6)–C(1′)–C(6′)–C(6′)H	−0·8(10)
C(2′)–C(1′)–C(6′)–C(5′)	−1·1(2)
C(2′)–C(1′)–C(6′)–C(6′)H	179·7(10)
C(1′)–C(2′)–C(3′)–C(4′)	−0·5(2)
C(1′)–C(2′)–C(3′)–C(3′)H	178·9(11)
C(2′)H–C(2′)–C(3′)–C(4′)	178·7(10)
C(2′)H–C(2′)–C(3′)–C(3′)H	−0·7(15)
C(2′)–C(3′)–C(4′)–C(5′)	−1·1(2)
C(2′)–C(3′)–C(4′)–C(4′)H	178·4(12)
C(3′)H–C(3′)–C(4′)–C(5′)	178·2(11)
C(3′)H–C(3′)–C(4′)–C(4′)H	−0·9(16)
C(3′)–C(4′)–C(5′)–C(6′)	−0·6(2)
C(3′)–C(4′)–C(5′)–C(5′)H	178·9(11)
C(4′)H–C(4′)–C(5′)–C(6′)	−177·9(12)
C(4′)H–C(4′)–C(5′)–C(5′)H	−1·5(17)
C(4′)–C(5′)–C(6′)–C(1′)	0·5(2)
C(4′)–C(5′)–C(6′)–C(6′)H	−179·1(10)
C(5′)H–C(5′)–C(6′)–C(1)′	−180·0 *
C(5′)H–C(5′)–C(6′)–C(6′)H	1·4(16)

* Angles in the form I–J–K–L, signed down J–K vector with J closest to eye; positive represents vector K–L clockwise from vector J–I, negative vector K–L counterclockwise from vector J–I. The function used to evaluate the σ values for dihedral angles is unreliable below *ca.* 0·05°. See also footnote in text.

significantly different from the C–N bond lengths which we find for (I). However, in light of the more probable σ values of 0·01 Å and 1·0° quoted in ref. 5,* there is no significant difference between the C–N bond lengths and the C–N–C bond angles of (I) and (II). By comparison, all these molecules do have bond lengths significantly different from the values for the C–N bond of pyridine [1·340(5) Å] and the C–N–C angle (116·7°).[16]

The dihedral angles of (I) are given in Table 4.† There are four dihedral angles of particular interest in this molecule. These are the phenyl twist around C(1′)–C(6), the biphenyl twist about C(12A)–C(12B), the benzil twist about C(6)–C(7) and the imine twist about C(4A)–N(5). Of the four, the most interesting is the second which is −57·0(2)°. This is in fair agreement with the gas-phase angle obtained by electron diffraction studies in biphenyl (41·6°).[17]

As can be seen from the unit-cell diagram (Figure 2), the molecules are tightly packed. Burgi and Dunitz[5] report no intermolecular carbon–carbon contacts <3.5 Å, whereas in (I) C(4′) approaches C(11) and C(12) of the molecule related to the *b* glide and translated one cell along *x* and one along −*y* to *ca.* 3·45 Å; and C(4″) approaches C(1) and C(2) of this molecule related by the *b* glide by 3·47 Å. Furthermore, Burgi and Dunitz find no intermolecular contacts of less than van der Waals radii. In (I), C(11)H and C(3′)H of the molecule translated one unit cell along −*y* are 2·42(2) Å apart. There are a total of 24 intermolecular contacts of less than 3 Å.

In addition, C(1)H and C(12)H have an intramolecular approach distance of 2·74 Å. In the planar transition-state envisaged earlier,[4] these are the two hydrogens which must push past each other. Even at the twist angle of 57° found in (I), these two hydrogens are already within the H–H van der Waals radii.

As would be expected, the phenyl rings each form a plane with a maximum deviation of 0·005 Å. The benzo-ring forms a plane with a maximum deviation of 0·015 Å. The nitrogen attached to the benzo-ring, however, deviates from the plane by 0·14 Å.

[3/751 *Received, 9th April,* 1973]

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* See p. 1757 of ref. 5. Experimental difficulties encountered by Burgi and Dunitz [libration, maximum $\theta = 25°$, very thin crystal (0·05 mm) and low m.p. (47—49°)] do not occur with (I) [small, nearly spherical thermal parameters, maximum $\theta = 65°$, block-like crystal, and high m.p. (236—238°)].

† σ Values quoted for the dihedral angles have been calculated by evaluation of the square root of the sums of squares of the 12 partials involved in the dihedral angle function multiplied by their σ values.

[16] B. Bak, L. Hansen, and J. Rastrup-Anderson, *J. Chem. Phys.*, 1954, **22**, 2013.

[17] O. Bastiansen and M. Traetteberg, *Tetrahedron*, 1962, **17**, 147.