5. Interactions between Functional Groups

Part I

Crystal Structure of 2-Phenylethynyl-*N*,*N*-dimethylaniline at 98 K: A Remarkably Short C–H···C Distance

by **John D. Wallis** and **Jack D. Dunitz***

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich

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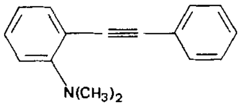
Summary

In the crystal structure of the title compound at 98 K the dimethylamino group has pyramidal geometry. The nitrogen lone pair is not directed towards the triple bond; instead, one $N-CH_3$ bond lies almost in the plane of the disubstituted ring, directed away from the triple bond, while the other $N-CH_3$ bond and the lone pair are directed to opposite sides of the plane, nearer to the acetylene. There is a remarkably short intramolecular contact (2.39 Å) between a methyl H- and an acetylenic C-atom. The *Taft* σ_I parameter of the arylethynyl substituent appears to be similar to that of a carboxylic ester, judging from the bond-angle deformation at the *ipso*-C-atom.

Introduction. – Interactions between neighbouring functional groups can often be regarded as representing incipient stages of chemical reactions [1–3]. We have now determined the crystal structure of the *ortho*-substituted tolane **1** at 98 K to investigate the nature of the interaction between the dimethylamino group and the adjacent C≡C bond.



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Discussion. – The molecular structure of **1** is shown in *Fig. 1* and relevant interatomic distances and angles are given in *Fig. 2*. The estimated standard deviations (e.s.d.'s) in bond lengths are 0.002–0.003 Å, but these estimates do not include any systematic errors that may be present. The main source of systematic error is probably the effect of rigid-body libration and possibly internal molecular motion, which causes most bond distances to appear shortened by *ca.* 0.001–0.002 Å (but 0.005 Å for the

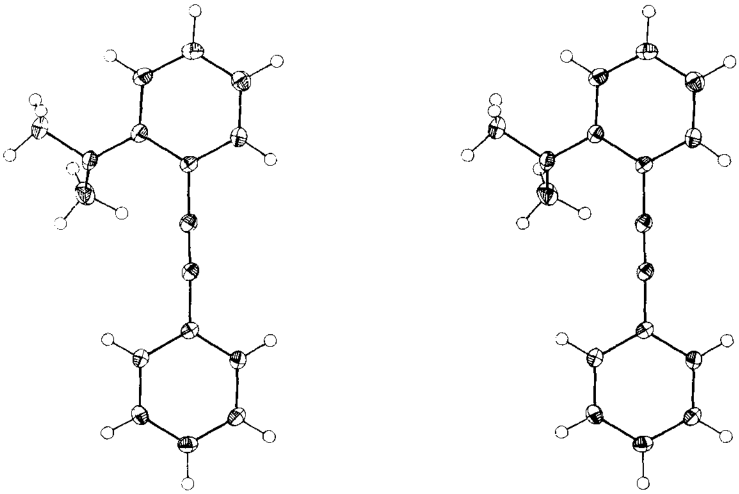

Fig. 1. *Stereographic view of* **1** *with vibrational ellipsoids at the 50% probability level* [31]

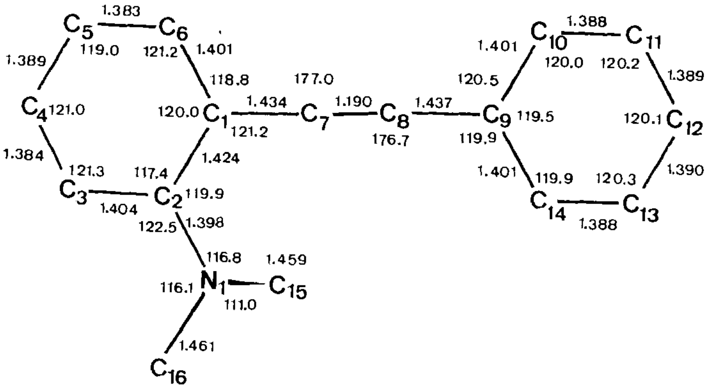

Fig. 2. *Bond lengths* (Å) *and bond angles* (°) *for* **1**

N–CH$_3$ bonds!). Bond angles are hardly affected. Another factor is the preponderance of low-order reflections in the least-squares refinement, based on intensity data extending only to $\sin\theta/\lambda \approx 0.64\,\text{Å}^{-1}$. This could result in C(7) and C(8) being slightly displaced towards the electron density of the triple bond, thus shortening the apparent C(7)–C(8) distance and lengthening the neighbouring C(1)–C(7) and C(8)–C(9) distances.[1]) The use of a modified weighting system [4] did not lead to any appreciable changes in these distances.

As can be seen from *Fig. 1* the dimethylamino group is pyramidal at the N-atom (sum of angles: 343.9°). Its conformation is such that one N–CH$_3$ bond is almost

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[1]) For tetrafluoroterephthalonitrile (data extending to $\sin\theta/\lambda \approx 1.15\,\text{Å}^{-1}$) the corresponding error for the C≡N bond amounts to about 0.01 Å when only reflections out to $\sin\theta/\lambda = 0.65\,\text{Å}^{-1}$ are used in the refinement [5].

antiperiplanar to the C(1)–C(2) bond of the benzene ring (C(16) lies 0.25 Å from the best plane through the ring) while the other N–CH_3 bond and the lone pair are synclinal to it. The C(1)–C(2)–N(1)–C(15) torsion angle is –60.4° and the C(1)–C(2)–N(1)–C(16) torsion angle is 165.6°. The C(2)–N(1) bond length of 1.398 Å is intermediate between the value of 1.36(2) Å observed for *N,N*-dimethylaniline derivatives with planar geometry at N[2]) and that of 1.43(1) Å for molecules with pyramidal N where the lone pair axis lies in the aromatic plane [2]. Both CH_3-groups are involved in close intramolecular contacts: C(15) and H(151) lie 3.03 Å and 2.39 Å, respectively, from the acetylenic C-atom C(7), while C(16) lies 2.45 Å from the *ortho*-H-atom H(31) and 2.80 Å from C(3). The angle between the least squares planes of the benzene rings is 18°.

The H(151) · · · C(7) distance of 2.39 Å is remarkably short for a 1,6(C)H · · · C interaction. Indeed, we have not been able to find any significantly shorter ones in published molecular structures, even in such overcrowded molecules as 1,2-di(*t*-butyl) aromatics.[3]) Equally short 1,6(C)H · · · C distances between phenyl H-atom and CN-group C-atoms have been observed in the structures of α-cyanocinnamates [12]; here the bond angle expansion at some of the intervening trigonal C-atoms (some to more than 130°) expresses the repulsive nature of these 1,6-interactions. On the other hand, the much shorter 1,6 (O)H · · · C distances of 2.11 and 2.16 Å in a 10-hydroxytricyclo[4.2.1.1^{2,5}]deca-3,7-diene derivative have been attributed to OH · · · π H-bonding [13]. Similar H-bonds to the π-density of C≡C bonds have been postulated from IR spectroscopic evidence and also to explain the abnormally low boiling point of 2-hydroxyphenylacetylene [14].

However, before we jump to any conclusions about the nature of the H(151) · · · C(7) interaction we should examine the possible alternative conformations available to the dimethylamino group. These are shown in *Fig. 3*. Conformations **b** and

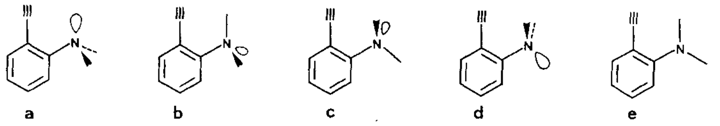

Fig. 3. *Five possible conformation for the dimethylamino group in* **1**

e have distances of only about 2.5 Å between a methyl C-atom and an acetylenic C-atom and are thus strongly disfavoured on steric grounds. Conformation **a** with the lone pair in the plane of the benzene ring is presumably disfavoured by repulsion between the lone pair and the π-density of the triple bond, besides the complete loss of conjugation. Of the remaining conformations, **d** has two short 1,6H · · · C interactions of the type found in our structure, while the observed conformation **c** has one. The

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[2]) Based on structural data obtained from a search of the *Cambridge Crystallographic Database* [6].

[3]) For 1,2,4,5-tetra(*t*-butyl)benzene [7], 2,3-di(*t*-butyl)quinoxaline [8] and 4,5-di(*t*-butyl)imidazole [9] 1,6(C)H · · · C distances lie in the range 2.58–2.98 Å though there are some shorter 1,7(C)H · · · C ones: 2.44–2.57 Å. In 2,2′,4,4′,6,6′-hexa(*t*-butyl)benzil [10] and *N*-methyl-*N*-benzyl-2,4,6-tri(*t*-butyl)benzamide [11] the shortest 1,6(C)H · · · C distances, between methyl H-atom and carbonyl C-atom, are 2.40–2.56 Å, only slightly larger than in **1**.

occurrence of **c** rather than **d** thus suggests that the 1,6H $\cdots$ C distance of 2.39 Å cannot correspond to a strong attraction. Even if it corresponds to a repulsion, the observed conformation can still be regarded as the energetically least unfavourable of the possibilities available.

Steric repulsion between the C(15) CH_3-group and the acetylene C-atom, C(7), is indicated by the displacement of C(7) by 0.145 Å from the least-squares plane through the disubstituted benzene ring on the opposite side to C(15). The ring itself is significantly nonplanar, (the main deviations being those of C(1) and C(2): 0.021 and -0.025 Å) in contrast to the monosubstituted ring, which is planar to within 0.005 Å. However, the repulsion in question cannot be very severe, as indicated by the relatively small deviation of the C(2)–C(1)–C(7) angle from its natural value. The repulsion on the C(15) side of the dimethylamino group is balanced by a repulsion of similar magnitude⁴) on the other side, due to interaction of the C(16) CH_3-group with H(31) and C(3). The effect of the latter repulsion is evident in the exocyclic bond angles at C(2).

The C(7) $\cdots$ H(151) distance depends on the conformation of the C(15) CH_3-group, which is rotated by $-18°$ from the ideal staggered orientation, where C(7) $\cdots$ H(151) would reach a minimum value of 2.36 Å. Rotation of this CH_3-group by $-42°$ to bring it into an eclipsed orientation would increase the shortest H $\cdots$ C(7) distance to about 2.85 Å, thus alleviating the steric repulsion, but only at the cost of the bond rotation barrier.⁵)

Substituent Effects. – According to *Domenicano & Murray-Rust* [17] substituents on benzene rings can be associated with characteristic angular distortion parameters, which, in turn, can be correlated with *Taft*'s substituent parameter σ_I. For the monosubstituted benzene ring in **1**, the observed bond angles (and bond distances) are symmetrical with respect to the line joining the *ipso-* and *para-*C-atoms. The angular deviations are small: $\Delta\alpha = -0.5$, $\Delta\beta = 0$, $\Delta\gamma = +0.25$, $\Delta\delta = +0.1°$, with e.s.d.'s of 0.1–0.2° (see *Fig. 4* for identification of symbols). Similar values were found in the room-temperature structure of tolane [18], but there are no accurate measurements of $\Delta\alpha$ for the unsubstituted ethynyl group for comparison. The $\Delta\alpha$-value of $-0.5°$ suggests that the arylethynyl substituent has a σ_I-value rather similar to that of the carboxylic ester group ($\Delta\alpha = -0.6°$) and greater than that of the methyl ($\Delta\alpha = -1.9°$) or ethenyl groups ($\Delta\alpha = -1.8°$) [17]. Note that σ_I-values may depend more on field effects than on

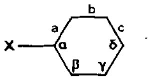

Fig. 4. *Labelling of bonds and angles for a monosubstituted benzene*

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⁴) Since certain important interactions are not adequately modelled in available force-fields we have not attempted to carry out a full molecular mechanics calculation. However, a rough calculation with the MM2 force-field [15] gives values of 1.6 and 1.7 kcal mol^{-1} for the two interaction energies (sums of C...C and H...C *van der Waals* energies).

⁵) A value of *ca.* 2 kcal mol^{-1} (as in methylamine [16]) for this energy quantity would be greater than the relief of *van der Waals* repulsion energy as estimated from the MM2 force-field [15].

through-bond inductive effects [19] since there seems to be little if any correlation between σ_I-values and parameters claimed to represent group electronegativities.

Additivity of angular substituent parameters cannot be taken for granted [17]. Nevertheless, for the disubstituted ring we assume that the angular distortion contribution from the phenylethynyl substituent at C(2) is negligible, leading to a $\Delta\alpha$-value of $-2.6°$ for the pyramidal dimethylamino group. We obtain the same value for the planar dimethylamino group by averaging $\Delta\alpha$-values from four low-temperature studies: 4-(dimethylamino)benzyl-4-(nitrophenyl)sulfone [20], 4-(dimethylamino)phenyl-*N*-methyl-*N*-[4-(nitrophenyl)sulfonylmethyl]carbamate [21], 4-(dimethylamino)phenylpentazole [22] and trichostatin A [23].

Hardly any simple monosubstituted benzene derivatives have been studied by low-temperature X-ray crystallography. However, the above results suggest that angular substituent parameters can be estimated from one or two accurate low-temperature (*ca.* 100K) studies just as well as by averaging results of many room-temperature analyses, as previously. From low-temperature studies it may also be possible to derive analogous parameters describing characteristic influences of substituents on the bond distances in the benzene ring (a, b, c in *Fig. 4*) as well as on the angles. Any such influences would be extremely difficult to detect from results of room-temperature studies because of systematic errors in the apparent atomic positions due to the increased librational motion, the relative lack of measurable high-angle reflections, and deficiencies in the free-atom model. Taking a standard C–C bond distance of 1.396 Å for benzene [24] we obtain for the arylethynyl substituent: $\Delta a = +0.005$ Å, $\Delta b = -0.008$ Å, $\Delta c = -0.007$ Å, all fairly small, and, again assuming additivity, we get for the pyramidal dimethylamino group averaged values of $\Delta a = +0.020$ Å, $\Delta b = \Delta c = -0.002$ Å. It is too early to say if these distance deformations will be as characteristic of the substituents as the angular parameters.

Molecular Packing. – The packing of the eight molecules in the orthorhombic *Pbcn* unit cell is shown in *Fig. 5*. There are no very short or otherwise remarkable intermolecular contacts, the shortest of each type being: C(12)···C(16; $-x$, $1+y$, $0.5-z$), 3.38 Å; N(1)···H(14; $-x$, y, $0.5-z$), 2.63 Å; H(5)···H(12; x, $1-y$, $z-0.5$), 2.36 Å.

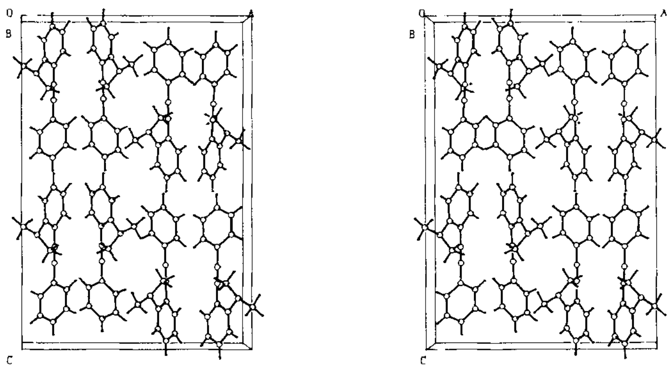

Fig. 5. *Stereographic view of the unit cell of* **1** [32]

Table. *Positional and Vibrational Parameters for* **1** (standard deviations in parentheses). The temperature factor expression is $\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots 2U_{12}hka^*b^*\ldots)]$ for non-H-atoms, $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$ for H-atoms.

Atom	X	Y	Z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.1455 (1)	0.1399 (3)	0.13465 (7)	0.0153 (7)	0.0180 (8)	0.0193 (8)	0.0015 (6)	−0.0012 (7)	−0.0034 (6)
C(2)	0.1048 (1)	−0.0285 (2)	0.11545 (8)	0.0136 (7)	0.0176 (8)	0.0229 (8)	0.0014 (6)	−0.0003 (6)	−0.0025 (6)
C(3)	0.1012 (1)	−0.0614 (3)	0.05483 (8)	0.0209 (9)	0.0225 (8)	0.0234 (9)	0.0010 (8)	−0.0013 (7)	−0.0067 (7)
C(4)	0.1400 (1)	0.0596 (3)	0.01536 (8)	0.0254 (9)	0.0300 (9)	0.0180 (8)	0.0025 (9)	−0.0011 (7)	−0.0036 (7)
C(5)	0.1836 (1)	0.2184 (3)	0.03450 (9)	0.0240 (9)	0.0255 (9)	0.0242 (9)	0.0006 (8)	−0.0002 (7)	0.0030 (8)
C(6)	0.1855 (1)	0.2581 (3)	0.09383 (8)	0.0201 (8)	0.0171 (8)	0.0251 (9)	−0.0015 (7)	−0.0008 (7)	0.0008 (7)
C(7)	0.1436 (1)	0.1958 (2)	0.19507 (8)	0.0169 (8)	0.0200 (8)	0.0228 (8)	−0.0007 (7)	−0.0023 (7)	−0.0011 (7)
C(8)	0.1423 (1)	0.2504 (2)	0.24439 (8)	0.0179 (8)	0.0170 (8)	0.0212 (8)	0.0004 (7)	−0.0012 (6)	−0.0017 (6)
C(9)	0.1403 (1)	0.3054 (2)	0.30502 (7)	0.0180 (7)	0.0153 (8)	0.0177 (7)	0.0023 (7)	−0.0029 (6)	−0.0009 (6)
C(10)	0.1978 (1)	0.4398 (3)	0.32650 (8)	0.0194 (8)	0.0203 (8)	0.0211 (8)	−0.0035 (7)	−0.0003 (6)	0.0002 (7)
C(11)	0.1967 (1)	0.4885 (3)	0.38544 (8)	0.0235 (9)	0.0193 (8)	0.0226 (9)	−0.0032 (7)	−0.0037 (7)	−0.0035 (7)
C(12)	0.1378 (1)	0.4061 (3)	0.42313 (7)	0.0263 (9)	0.0227 (9)	0.0169 (8)	0.0015 (8)	−0.0029 (7)	−0.0009 (6)
C(13)	0.0799 (1)	0.2742 (3)	0.40195 (8)	0.0217 (8)	0.0197 (9)	0.0206 (8)	−0.0001 (7)	0.0010 (7)	0.0048 (7)
C(14)	0.0809 (1)	0.2231 (2)	0.34322 (8)	0.0170 (7)	0.0162 (8)	0.0217 (8)	−0.0009 (6)	−0.0019 (7)	0.0005 (7)
C(15)	0.1214 (1)	−0.2272 (3)	0.20156 (9)	0.033 (1)	0.0270 (9)	0.0276 (9)	−0.0014 (8)	−0.0009 (8)	0.0079 (8)
C(16)	0.0088 (1)	−0.2912 (3)	0.1324 (1)	0.034 (1)	0.029 (1)	0.034 (1)	−0.0143 (9)	0.0015 (9)	−0.0035 (9)
N(1)	0.0662 (1)	−0.1481 (2)	0.15626 (7)	0.0199 (7)	0.0172 (7)	0.0253 (7)	−0.0041 (6)	0.0007 (6)	−0.0012 (6)
H(31)	0.074 (2)	−0.172 (4)	0.042 (1)	0.026 (6)					
H(41)	0.139 (2)	0.035 (4)	−0.027 (1)	0.025 (6)					
H(51)	0.213 (2)	0.301 (4)	0.005 (1)	0.032 (7)					
H(61)	0.212 (2)	0.368 (4)	0.109 (1)	0.024 (6)					
H(101)	0.238 (2)	0.493 (4)	0.300 (1)	0.031 (7)					
H(111)	0.235 (2)	0.581 (4)	0.399 (1)	0.022 (6)					
H(121)	0.138 (2)	0.443 (4)	0.464 (1)	0.025 (6)					
H(131)	0.038 (2)	0.223 (3)	0.426 (1)	0.011 (6)					
H(141)	0.040 (1)	0.135 (3)	0.3297 (9)	0.021 (5)					
H(151)	0.167 (2)	−0.131 (4)	0.215 (1)	0.044 (8)					
H(152)	0.089 (2)	−0.248 (5)	0.236 (2)	0.07 (1)					
H(153)	0.152 (2)	−0.352 (5)	0.186 (1)	0.06 (1)					
H(161)	−0.036 (2)	−0.229 (4)	0.107 (1)	0.040 (9)					
H(162)	0.042 (2)	−0.391 (4)	0.110 (1)	0.035 (7)					
H(163)	−0.018 (2)	−0.347 (4)	0.168 (1)	0.035 (7)					

Thermal Motion. – The molecule satisfies the rigid-body test [25] reasonably well except for the methyl C-atoms, C(15) and C(16). The agreement between observed and calculated thermal parameters obtained with the computer program THMB [26] was improved (weighted *R* reduced from 0.152 to 0.127) by inclusion of an internal rotation axis along the N(1)–C(2) bond and affecting the two methyl C-atoms. A value of 28 (5) deg^2 was obtained for the mean-square libration amplitude about this axis. In comparison, the mean-square amplitude of the largest rigid-body libration is 6.3 (2.5) deg^2, about a direction close to the long axis of the tolane system: the other two rigid-body librations are extremely small. It was not possible to detect the separate internal motions of the benzene rings.

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Experimental Part

2-Phenylethynyl-*N,N*-dimethylaniline, **1**, $C_{16}H_{15}N$, $M = 221.3$, was prepared by a literature method [27] and crystallized at –15° from MeOH. The pale yellow crystals are orthorhombic, space group *Pbcn*, $Z = 8$, with cell dimensions $a = 15.626(4)$, $b = 7.107(2)$, $c = 22.807(6)$ Å at 98 K ($a = 15.974(3)$, $b = 7.139(1)$, $c = 22.985(3)$ at 291 K). Intensity measurements were made at 98 K with an *Enraf Nonius CAD4* diffractometer equipped with a graphite monochromator (Mo$K\alpha$, $\lambda = 0.7107$ Å) and cooling device; 2761 independent reflections were measured out to $\theta = 27°$ of which 1696 with $I \geq 3\sigma\ (I)$ were used in the refinement. The structure was solved by the program MULTAN 80 [28] and refined by blocked-matrix least-squares analysis using the SHELX [29] and XRAY72 [30] programs. A modified weighting scheme [4] with $r = 5.0$ Å^2 was used in the final refinement cycles ($R = 0.043$, $R_W = 0.048$) leading to the atomic positional and vibrational parameters listed in the *Table*.

REFERENCES

[1] *H.B. Bürgi, J.D. Dunitz & E. Shefter,* J. Am. Chem. Soc. *95,* 5065 (1973); *M. Kaftory & J.D. Dunitz,* Acta Crystallogr. *B31,* 2912, 2914 (1975); *G. Procter, D. Britton & J.D. Dunitz,* Helv. Chim. Acta *64,* 471 (1981).

[2] *W.B. Schweizer, G. Procter, M. Kraftory & J.D. Dunitz,* Helv. Chim. Acta *61,* 2783 (1978).

[3] *J.D. Dunitz,* 'X-ray Analysis and the Structure of Organic Molecules', Cornell University Press, Ithaca, NY, 1979, Chapter 7.

[4] *J.D. Dunitz & P. Seiler,* Acta Crystallogr. *B29,* 589 (1973).

[5] *J.D. Dunitz, W.B. Schweizer & P. Seiler,* Helv. Chim. Acta *66,* 123 (1983).

[6] *F.H. Allen, O. Kennard & R. Taylor,* Acc. Chem. Res. *16,* 146 (1983).

[7] *C.H. Stam,* Acta Crystallogr. *B28,* 2715 (1972).

[8] *G.J. Visser & A. Vos,* Acta Crystallogr. *B27,* 1793 (1971).

[9] *G.J. Visser & A. Vos,* Acta Crystallogr. *B27,* 1802 (1971).

[10] *E.J. Gabe, Y. Le Page, F.L. Lee & L.R.C. Barclay,* Acta Crystallogr. *B37,* 197 (1981).

[11] *A.G. Jungk & G.M.J. Schmidt,* Chem. Ber. *104,* 3289 (1971).

[12] *H. Nakanishi & Y. Sasada,* Acta Crystallogr., *B34,* 332 (1978); *H. Nakanishi, K. Meno & Y. Sasada,* Acta Crystallogr. *B32,* 1616 (1976).

[13] *W.B. Schweizer, J.D. Dunitz, R.A.Pfund, G.M. Ramos Tombo & C. Ganter,* Helv. Chim. Acta *64,* 2738 (1981).

[14] *B. Jordanov, A. Jovtscheff, S. Spassov, B. Blagoev & M. Agova,* Tetrahedron *20,* 903 (1964); *V. Prey & H. Berbalk,* Monatsch., *82,* 990 (1951).

[15] *N.L. Allinger & Y.H. Yuh,* Program MM2, 1980.

[16] *E. L. Eliel,* 'Stereochemistry of Carbon Compounds', McGraw-Hill, New York, 1962, p. 134.

[17] *A. Domenicano & P. Murray-Rust,* Tetrahedron Lett. *1979,* 2283.

[18] *A. Mavridis & I. Moustakali-Mavridis,* Acta Crystallogr. *B33,* 3612 (1977); *A. A. Espiritu & J. G. White,* Z. Kristallogr. *147,* 177 (1978).

[19] *W. F. Reynolds,* J. Chem. Soc., Perkin Trans 2 *1980,* 985.

[20] *I. Tickle, J. Hess, A. Vos & J. B. F. N. Engberts,* J. Chem. Soc., Perkin Trans. 2 *1976,* 460.

[21] *R. J. J. Visser, A. Vos & J. B. N. F. Engberts,* J. Chem. Soc., Perkin Trans. 2 *1978,* 634.

[22] *J. D. Wallis & J. D. Dunitz,* J. Chem. Soc., Chem. Commun. *1983,* 910.

[23] *D. L. Eng-Wilmot & D. van der Helm,* Acta Crystallogr. *B37,* 718 (1981).

[24] *K. Tomagawa, T. Iijima & M. Kimura,* J. Mol. Struct. *30,* 243 (1976).

[25] *R. E. Rosenfield, K. N. Trueblood & J. D. Dunitz,* Acta Crystallogr. *A34,* 828 (1978).

[26] *V. Schomaker & K. N. Trueblood,* Acta Crystallogr. *B24,* 63 (1968).

[27] *R. W. M. Ten Hoedt, G. van Koten & J. G. Noltes,* J. Organomet. Chem. *170,* 131 (1979).

[28] *P. Main,* MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of York, England, 1980.

[29] *G. M. Sheldrick,* SHELX 76, System of Computing Programs, University of Cambridge, England, 1976.

[30] *J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson & S. R. Hall,* Technical Report TR 192, Computer Science Centre, University of Maryland, 1972.

[31] *C. K. Johnson,* Program ORTEP, Oak Ridge National Laboratory Report ORNL 3794, 1965.

[32] Program PLUTO, Cambridge Crystallographic Data Centre, University of Cambridge, England, 1979.