Molecular Structure of *p*-Nitrobiphenyl. A Comparison of the Results of *X*-Ray Crystal Analysis with Semi-empirical Calculations of Conformation

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The crystal and molecular structure of *p*-nitrobiphenyl has been determined from photographic *X*-ray data. Crystals are orthorhombic, space group *Pbca*, with $Z = 8$, in a unit cell of dimensions $a = 23{\cdot}210$, $b = 11{\cdot}370$, and $c = 7{\cdot}568$ Å. The crystal structure was solved by direct methods and has been refined by least-squares methods to R 0·067 for 1495 visually estimated reflections. The value of the dihedral angle between phenyl rings is 33°. Conformational analysis was carried on by the semi-empirical method both for the isolated molecule and for the molecule in the crystal; results were in fair agreement with those found experimentally.

A CHARACTERISTIC geometrical feature of biphenyl and its *para*-substituted derivatives is the dihedral angle between the phenyl rings. In the crystalline molecule of biphenyl[1,2] and 4,4′-dihydroxydiphenyl[3] the phenyl rings are coplanar, while in *p,p′*-bitolyl[4] and 4,4′-dinitrodiphenyl[5] they are rotated, the rotation angle being in the range 35—40°. The latter seems to be the optimal value for this angle, in the isolated molecule, of compounds which can allow phenyl ring rotation. In fact, it was found as a result of semi-empirical calculations performed on the 1,1-di-*p*-tolylethylene,[6] biphenyl,[1] and 1,1-di-(*p*-nitrophenyl)ethylene[7] molecules. A similar value was also obtained for gaseous biphenyl from electron diffraction experiments.[8]

TABLE 1

Non-hydrogen atom fractional parameters (all × 10^4) * with their standard deviations

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2066(1)	4089(3)	1737(5)	20(1)	104(3)	254(7)	11(1)	16(2)	21(4)
C(2)	2154(1)	3049(3)	837(5)	17(0)	92(2)	254(7)	−3(1)	3(1)	6(3)
C(3)	2705(1)	2727(2)	322(4)	18(0)	68(2)	198(6)	−2(1)	2(1)	−3(3)
C(4)	3178(1)	3453(2)	690(3)	16(0)	61(2)	149(5)	1(1)	0(1)	7(2)
C(5)	3076(1)	4508(2)	1584(4)	21(0)	67(2)	174(5)	2(1)	−1(1)	−5(2)
C(6)	2524(1)	4819(3)	2109(4)	24(1)	79(2)	199(6)	9(1)	9(1)	−9(3)
C(7)	3764(1)	3124(2)	105(3)	17(0)	60(2)	147(5)	0(1)	−5(1)	−3(2)
C(8)	3925(1)	1938(2)	13(4)	20(0)	62(2)	196(6)	1(1)	−2(1)	0(3)
C(9)	4467(1)	1617(3)	−565(4)	21(1)	75(2)	219(7)	7(1)	−5(1)	−11(3)
C(10)	4846(1)	2488(3)	−1056(4)	15(0)	101(2)	191(6)	3(1)	−4(1)	−18(3)
C(11)	4701(1)	3665(3)	−990(4)	19(1)	88(2)	217(7)	−3(1)	0(1)	−6(3)
C(12)	4162(1)	3974(2)	−402(4)	18(0)	69(2)	204(6)	−1(1)	0(1)	−2(3)
N	5417(1)	2161(3)	−1719(4)	17(0)	143(3)	304(7)	9(1)	−1(1)	−40(4)
O(1)	5546(1)	1127(3)	−1762(5)	24(1)	150(3)	576(11)	19(1)	17(2)	−92(5)
O(2)	5744(1)	2937(3)	−2194(5)	21(0)	184(4)	563(11)	0(1)	35(2)	17(5)

* The temperature factor is in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

We present here the results of a crystal structure investigation and conformational analysis of the *p*-nitrobiphenyl molecule as part of a study on biphenyl and its derivatives.[4,9]

EXPERIMENTAL

Crystals are parallelepipeds elongated along the c axis.

Crystal Data.—$C_{12}H_9NO_2$, $M = 199{\cdot}2$, m.p. 114°. Orthorhombic, $a = 23{\cdot}210 \pm 0{\cdot}004$, $b = 11{\cdot}370 \pm 0{\cdot}001$, $c = 7{\cdot}568 \pm 0{\cdot}002$ Å, $U = 1997$ Å^3, $D_m = 1{\cdot}327$ (by flotation), $Z = 8$, $D_c = 1{\cdot}325$, $F(000) = 832$. Space group *Pbca* from systematic absences. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 7·6 cm^{-1}.

Space group and cell parameters are in agreement with the results of an early crystallographic investigation.[10] Unit-cell parameters were obtained from a least-squares fit to measurements of $\sin^2\theta$ for 17 $hk0$ and 13 $0kl$ reflections on zero-level Weissenberg photographs held in position by the Straumanis technique. Intensity data were collected from multiple-film equi-inclination Weissenberg photographs taken with Ni-filtered Cu-K_α radiation. Intensities were estimated visually for the levels $hk0$—6 and 0—$3kl$. After correction for Lorentz and polarization effects, the data were scaled by a least-squares procedure.[11] Of a total of 2283 reflections within the effective sphere of Cu-K_α radiation, 1998 independent reflections were obtained, of which 473 were considered too weak to be measured.

Structure Solution and Refinement.—The structure was solved by direct methods. 212 Reflections with $E > 1{\cdot}5$ were used as input for Long's program for sign determination.[12] The solution with the highest consistency index, which was also the one which converged most rapidly,

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afforded an E map which clearly revealed the positions of the fifteen heavy atoms.

The structural parameters were refined by least-squares methods the quantity minimized being $\Sigma w(|F_o| - |F_c|)^2$. Hydrogen atom positions were revealed by a difference-Fourier synthesis, computed after allowance for anisotropic thermal motion of the heavy atoms. The hydrogen atoms were refined with isotropic temperature factors. In the final full-matrix least-squares cycles weights were assigned as $w^{-1} = a + b|F_o| + c|F_o|^2$, where a, b, and c were obtained from a least-squares fit of $(|F_o| - |F_c|)^2$ as a function of $|F_o|$. Of the 1525 measured intensities, 30 were given zero-weight as being affected by extinction or other observational errors. The final value of R was 0·067 for the 1495 observed reflections having non-zero weight.

The final heavy-atom and hydrogen atom parameters are given in Tables 1 and 2 respectively, together with their standard deviations as derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20580 (13 pp., 1 microfiche).*

TABLE 2

Fractional parameters for hydrogen atoms with their standard deviations

	x	y	z	$10B/\text{Å}^2$
H(1)	0·170(2)	0·430(3)	0·204(5)	38(8)
H(2)	0·184(1)	0·252(3)	0·061(4)	29(7)
H(3)	0·276(1)	0·202(3)	−0·028(4)	27(7)
H(4)	0·341(2)	0·501(3)	0·190(4)	33(7)
H(5)	0·246(2)	0·552(3)	0·282(5)	44(9)
H(6)	0·363(1)	0·130(3)	0·022(4)	30(7)
H(7)	0·459(1)	0·077(3)	−0·054(4)	28(7)
H(8)	0·495(2)	0·422(3)	−0·141(5)	38(8)
H(9)	0·405(1)	0·480(3)	−0·037(4)	25(6)

Minimum-energy Geometry of the Isolated Molecule.—Energy minimization calculations based on an extended Westheimer method [9,13] were carried on in order to find the best geometry of the isolated molecule of *p*-nitrobiphenyl. All bond angles were assumed to be 120°, and C–C(phenyl ring), C–H, C–N, and N–O bond lengths were taken as 1·397, 1·08, 1·47, and 1·22 Å.[7] The energy was calculated as the sum of various contributions:

$$E = E_\pi + E_s + E_{nb}$$

and was minimized with respect to the following three internal degrees of freedom: the C(4)–C(7) bond distance d, the dihedral angle ϕ between the phenyl rings, and the rotation angle ψ of the nitro-group with respect to the attached phenyl ring. The various energy terms were computed as follows.

π-Electron Energy.—The energy E_π for the 16 π-electrons was evaluated by the Hückel method with the following set of parameters: α_N 1·1β_o, α_O 0·7β_o, and β_{N-O} β_o, where β_o is 30 kcal mol^{-1}.[8] The resonance integral β_{C-N} was considered to be a function of ψ, and set equal to 0·5β_o cos ψ. The dependence of $\beta_{C(4)-C(7)}$ from ϕ and d was taken into account by means of the appropriate Mulliken formula.[14]

Stretching Energy.—The term E_s was calculated for the C(4)–C(7) bond according to the expression $E_s = \frac{1}{2}k_s(d - d_0)^2$ where the values of k_s and d_0 were taken from ref. 9.

Non-bonded Interaction Energy.—The energy E_{nb} was evaluated as the sum of the interactions between all non-bonded atom pairs. For C · · · C, C · · · H, and H · · · H interactions, Bartell's formulae were used.[15] Potential curves determined recently by Mirskaya and Nautchitel and reported in ref. 16 were used for N · · · N, N · · · C, and N · · · H interactions. Kitaigorodsky's formula [17] was used for the remaining interactions and the values of 1·7, 1·6, 1·5, and 1·5 Å were adopted as van der Walls radii for carbon, nitrogen, oxygen, and hydrogen atoms.

TABLE 3

Details of the minimum-energy calculations for the isolated molecule

Variable	Range	Scanning interval
d	1·46—1·54 Å	0·02 *
ϕ	0—90°	10 †
ψ	0—10°	2

* 0·01 Å From 1·48—1·52 .Å † 1° From 30—40°.

The details of these calculations are reported in Table 3. The minimum-energy geometry for the isolated molecule was found for the following values of the variables: d 1·51 Å, ϕ 35°, and ψ 0°.

RESULTS AND DISCUSSION

The arrangement of the molecules in the crystal is shown in Figure 1, together with the numbering of the atoms.[18] It is evident, from the drawing that there is pronounced anisotropy of the oxygen atoms.

Bond lengths and bond angles (Tables 4 and 5) are in good agreement with those reported in the literature.

TABLE 4

Bond distances (Å)

C(1)–C(2)	1·380	C(8)–C(9)	1·383
C(2)–C(3)	1·387	C(9)–C(10)	1·376
C(3)–C(4)	1·401	C(10)–C(11)	1·380
C(4)–C(5)	1·397	C(11)–C(12)	1·375
C(5)–C(6)	1·388	C(12)–C(7)	1·391
C(6)–C(1)	1·378	C(10)–N	1·465
C(4)–C(7)	1·479	N–O(1)	1·214
C(7)–C(8)	1·401	N–O(2)	1·218

TABLE 5

Bond angles (deg.)

C(1)–C(2)–C(3)	120·1	C(7)–C(8)–C(9)	120·8
C(2)–C(3)–C(4)	120·7	C(8)–C(9)–C(10)	118·5
C(3)–C(4)–C(5)	118·1	C(9)–C(10)–C(11)	122·2
C(3)–C(4)–C(7)	120·8	C(9)–C(10)–N	119·2
C(5)–C(4)–C(7)	121·2	C(11)–C(10)–N	118·6
C(4)–C(5)–C(6)	120·9	C(10)–C(11)–C(12)	118·8
C(5)–C(6)–C(1)	120·0	C(11)–C(12)–C(7)	121·1
C(6)–C(1)–C(2)	120·2	C(10)–N–O(1)	118·6
C(4)–C(7)–C(8)	120·2	C(10)–N–O(2)	118·7
C(4)–C(7)–C(12)	121·1	O(1)–N–O(2)	122·7
C(12)–C(7)–C(8)	118·6		

The evaluated standard deviations range from 0·003—0·005 Å for bond distances and from 0·2 to 0·3° for bond angles. Carbon–hydrogen bond lengths are in the range 0·91—1·01 Å.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

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The mean planes in the molecule, determined according to the method of ref. 19 are reported in Table 6. The nitro-group is coplanar with the attached phenyl ring, as expected. The experimental value of the dihedral angle ϕ between phenyl rings is 33°, which is very close both to that calculated for the isolated molecule and to those found for crystalline molecules of similar compounds. This fact could suggest that packing forces do not change the conformation considerably from that in an isolated molecule to that in a crystal.

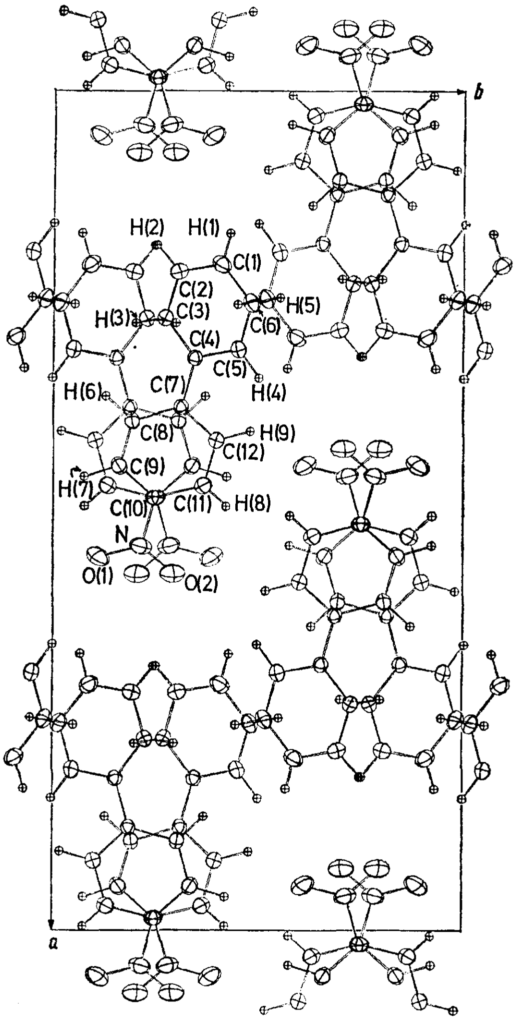

FIGURE 1 Arrangement of the molecules in the crystal as viewed along the c axis. Thermal ellipsoid plot at a probability 0·20. Hydrogen atoms, treated as isotropic, are on an arbitrary scale.

Intermolecular distances are in the normal range. There are only two $C \cdots H$ contacts (2·87 and 2·77 Å) shorter than the sum of van der Waals radii (r_C 1·7 and r_H 1·2 Å[20]). To get a better understanding of this problem, semi-empirical calculations were performed in order to find the minimum-energy conformation for the molecule in the crystal. The energy per molecule in the crystal was evaluated as the sum of the energy of the isolated molecule plus the packing energy. The latter was calculated as one half of the sum of non-bonded interaction energies for atom pairs with one atom in the reference molecule and one atom in an adjacent molecule. These calculations were carried out according to the method of ref. 7. The reference molecule was given the following internal degrees of freedom: the dihedral angles ϕ' and ϕ'' of the first and second phenyl ring with respect to the same ring in the experimental conformation. Results are shown in Figure 2, from which it appears that the most stable conformation is very close

TABLE 6

Mean planes

The coefficients q_i are the direction cosines relative to the crystallographic axes a, b, and c, and D(Å) is the distance from the origin. Relevant distances (Å) of atoms from the planes are given in square brackets.

	q_1	q_2	q_3	D
Plane (1):				
C(1)—(6)	−0·1355	0·4715	−0·8714	−0·401
[C(7) 0·022, C(10) 0·106, N 0·188]				
Plane (2):				
C(7)—(12)	0·3424	0·0480	0·9383	−3·236
[C(1) −0·137, C(4) −0·033, N −0·033]				
Plane (3):				
C(10), N, O(1), O(2)	0·3675	0·0656	0·9277	−3·577

Angles between planes (deg.):

ϕ, (1)–(2)	33
ψ, (2)–(3)	2

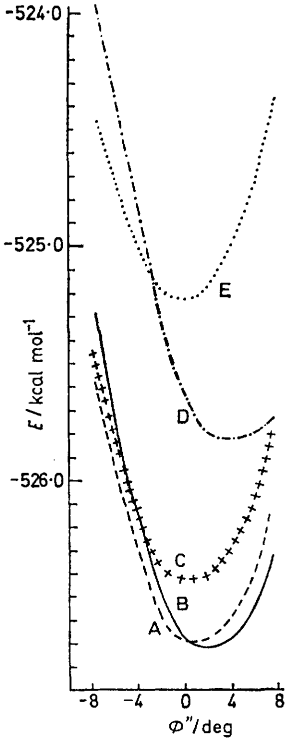

FIGURE 2 Total energy of the molecule in the crystal as a function of ϕ' and ϕ''. Values of ϕ' are: A, 0; B, 3; C, −2; D, 8; and E, −7°

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[20] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960.

to the experimental one, since the corresponding dihedral angle ϕ between phenyl rings is 32°. The molecule as a whole is only slightly rotated by 2·5° with respect to the experimental conformation. This is a further confirmation that, in spite of the many assumptions, this method of conformational analysis is essentially correct both for the isolated molecule and for the molecule in the crystal. On conclusion of this and previous similar investigations, it seems reasonable to infer that the value of *ca.* 35° for the dihedral angle between phenyl rings is a rather typical feature of the isolated molecule of *para*-substituted biphenyls, whatever is the substituent. This means that variations of π-electron energy with the dihedral angle are closely parallelled in different compounds.

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