Crystal, Molecular and Electronic Structure of 1,1-diaryl-2-halogenoethylenes

III. Semiempirical Calculations on the Crystal, Molecular and Electronic Structure of 2-bromo-1,1-diphenylprop-1-ene[*]

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On the basis of semiempirical calculations, the conformation of the isolated molecule of 2-bromo-1,1-diphenylprop-1-ene corresponding to the minimum of total energy was determined. Assuming some information on the localization of the molecules in the crystal, also the conformation in a *theoretical* crystal was studied. The results have been compared with the crystal structure of 2-bromo-1,1-diphenylprop-1-ene, as obtained by X-ray diffraction. From the comparison a slight displacement of the C2 atom was suggested.

Die dem Minimum der Gesamtenergie entsprechende Konformation des isolierten Moleküls von 2-Brom-1,1-diphenylprop-1-en wurde durch halb-empirische Methoden bestimmt. Gewisse Ergebnisse über die Anordnung der Moleküle im Kristall machten es möglich, die Konformation in einem *theoretischen* Kristall zu untersuchen. Nach Vergleich der Resultate mit der durch Röntgen-Analyse bestimmten Kristallstruktur des 2-Brom-1,1-diphenylprop-1-en wurde eine kleine Verschiebung des C2-Atoms vorgeschlagen.

Par le moyen de calculs semiempiriques on a déterminé la conformation de la molécule isolée de 2-bromo-1, 1-diphénilprop-1-ène, correspondant au minimum d'énergie totale. On a aussi étudié la conformation dans le cristal *théorique* en se basant sur des informations concernant la localisation des molécules dans le cristal. On a comparé ces résultats avec ceux que nous avons obtenus par la détermination de la structure cristalline du 2-bromo-1, 1-diphénilprop-1-ène avec la diffraction des rayons X: cette comparaison nous a porté à déplacer un petit peu l'atome C 2.

Introduction

The crystal and molecular structure of 2-bromo-1,1-diphenylprop-1-ene has been recently investigated by means of X-ray diffraction [2]. There are four formula units in the monoclinic cell, with parameters $a = 5.97$, $b = 16.97$, $c = 12.63$ Å, $\beta = 103.7°$ and space group $P2_1/c$. After anisotropic refinement by full-matrix least squares technique the final reliability index was $R = 8.5\%$.

The intramolecular angles and distances are shown in Fig. 1; Fig. 2 shows a view along the x axis of a reference molecule F together with molecules for which intermolecular distances equal to or less than the *touching* distance may appear.

Benzenic hydrogen atoms were assumed to lie on the line bisecting the angle between the two C–C bonds from the same carbon atom, with the carbon-hydrogen

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C1 1.57 110 1.92 Br
C2 $\phi_4=128$ $\phi_3=122$
H6 1.31
$\phi_1=119$ C3 $\phi_2=128$
H1
C11 1.41 114 1.49
H7 1.38 122 1.49 C5
C12 121 C10 123 1.40 121
119 117 121 $\theta_1=71$ $\theta_2=47$ 119 118 C4 H2
1.39 1.39 1.38 120 C6
C13 120 122 C15 H10 1.38
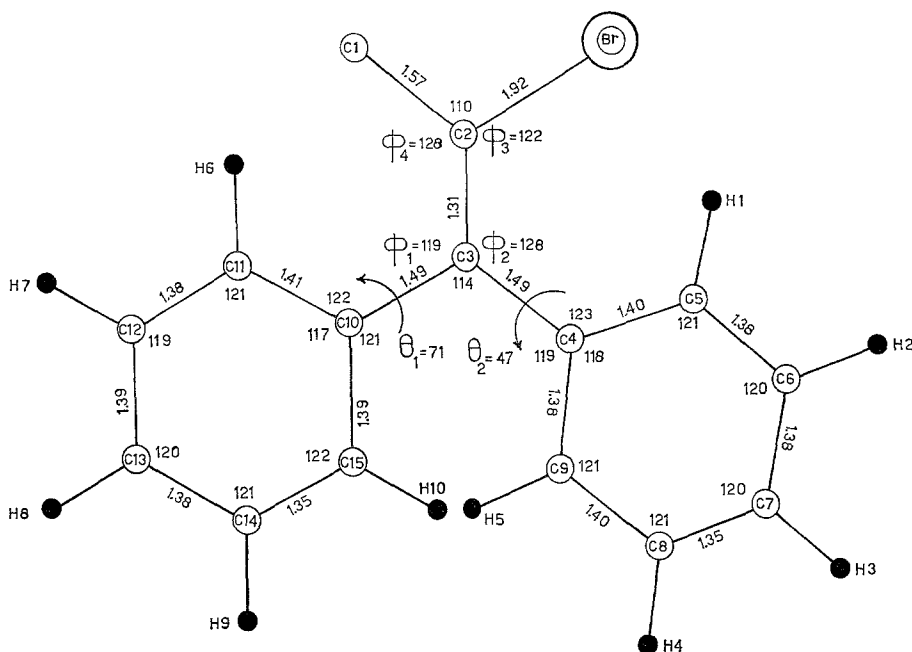H8 121 1.35 H5 C9 121 120 C7
C14 1.40 121 H3
H9 C8 1.35
H4

Fig. 1. Experimental angles (degrees) and bond distances (Å)

bond distance equal to 1.08 Å. The positions of the hydrogen atoms of the methyl group were not determined.

Since both the ethylenic and the $C_{ethylenic} - C_{methyl}$ bond distances were significantly different from expected values, theoretical calculations were undertaken to see if the crystal and molecular structure could be corrected without conflict with the experimental data.

The procedure to accomplish this theoretical investigation was analogous to the one used in the case of 2-bromo-1,1-di-p-tolylethylene [3].

Calculations

All the calculations were carried out on an IBM 1620-20K electronic computer.

The first step was the determination of the geometry for an isolated molecule by minimization of the energy with respect to the following parameters: ϑ_1, ϑ_2, φ_1, φ_2, φ_3, φ_4, d_{C-CH_3} (C2–C1 distance) and d_{C-Br} (C2–Br distance).

The energy was calculated as the sum of the following items: π-electron energy, bending energy of the σ bonds starting from the ethylenic carbons, intramolecular steric repulsion, stretching or compression energy along the C1–C2 bond.

The π-electron energy was calculated for $\vartheta_1 = 45, 55, 65, 75, 85°$ and $\vartheta_2 = 25, 35, 45, 55, 65°$ by the Hückel molecular orbital (HMO) method using the ω-technique. Details of how bromine and methyl group were included and how bond lengths were obtained from bond orders are described in Ref. [3]: the same procedure was exactly followed here. Since all the C–C distances in the two aromatic rings for all cases were in the range 1.396 – 1.404 Å, the two rings were assumed to be regular hexagons with a side of 1.40 Å.
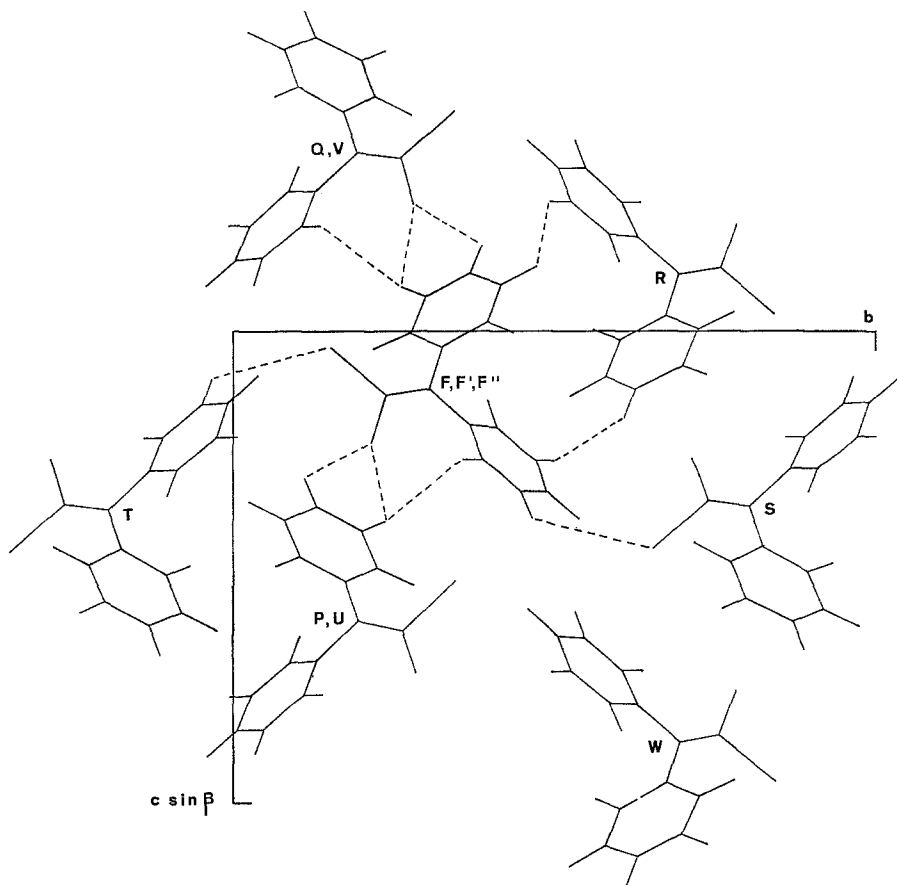
Fig. 2. Packing of molecules viewed along the x axis. The meaning of the labels for different molecules are explained in Tab. 1

The repulsion energy for pairs of atoms at distances smaller than the *touching* distance and the bending energy in the plane of the bonds were also calculated following the prescription given in Ref. [3]. For each φ_i at least three values scanned by 5° were tried, in the range 115 — 130°. The value used for the force constant k_4 was $0.93 \cdot 10^{-11}$ erg/rad² [5].

Owing to the lack of information on the variation of β_{C-CH_3} with distance, its value was kept constant, that is independent from d_{C-CH_3} and equal to $0.8\,\beta_0$ in all the calculations.

The following values of d_{C-CH_3} were considered: 1.50, 1.52 (experimental value from *trans*-but-2-ene [7]), 1.54 and 1.56 Å.

The stretching or compression energy (in Kcal/mole) for this bond was taken care of by the Morse formula

$$E = 87.2 \{1 - \exp[2.05(1.52 - R)]\}^2$$

where the dissociation energy [1] and the force constant [4] were taken from the literature and the approximation $a = \sqrt{k/2D} = 2.05$ Å^{-1} was used.

For the C–Br bond the β value $0.4\,\beta_0$ was used at all distances and no correction for stretching or compression was included. The following values of $d_{\text{C–Br}}$ were tried: 1.87, 1.90, 1.92 Å. This made the total number of tried model molecules equal to 24 300.

The total energy for the crystal was obtained adding to the single molecule energy the packing energy. To evaluate this last contribution the following scheme was applied:

1. A model molecule was located approximately in the same position and orientation of the real reference molecule in the crystal, i.e. with the C3 atom, the C2–C3 axis and the C2, C3, C4, C10 plane coincident in both molecules.

2. The coordinates of the atoms of the surrounding model molecules were obtained by symmetry operations.

3. The packing energy was calculated as the sum of one half of the interaction energy for all pairs of atoms belonging to different molecules at distances smaller than the *touching* distance. No correction of Van der Waals radii was applied.

In this way a rough minimum for the function $E = E\,(\vartheta_1,\ \vartheta_2,\ \varphi_1,\ \varphi_2,\ \varphi_3,\ \varphi_4,\ d_{\text{C–CH}_3},\ d_{\text{C–Br}})$ was found. From this point, keeping $d_{\text{C–Br}}$ constant, a more refined minimum with respect to all the other variables was sought applying the method of RANSIL [6].

Assuming that thermal energy, entropy and attractive Van der Waals forces in the real crystal and in the model crystal are the same, the minimum of energy (isolated molecule plus packing) corresponds to the minimum of free energy.

With this assumption we can calculate the most stable geometry for the crystal, to be compared with the experimental results.

Results and Discussion

a) Isolated Molecule

The minimum of energy for an isolated molecule was obtained with the geometry shown in Fig. 3.

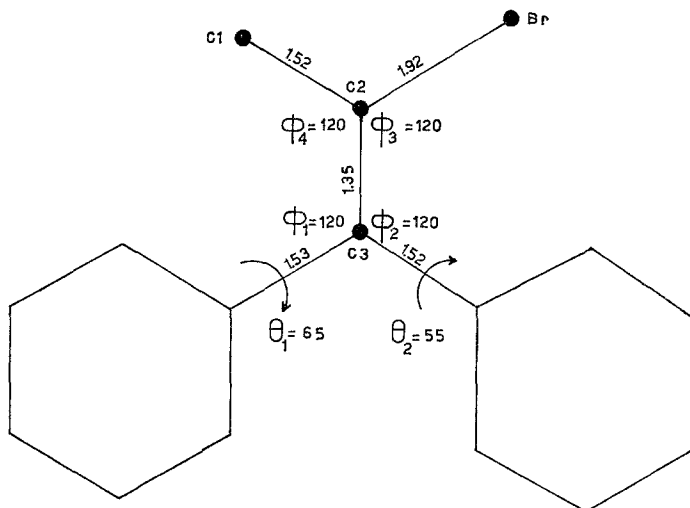All bond angles and distances were found to have values close to expectation.

Fig. 3. Geometry corresponding to the minimum energy for the isolated molecule
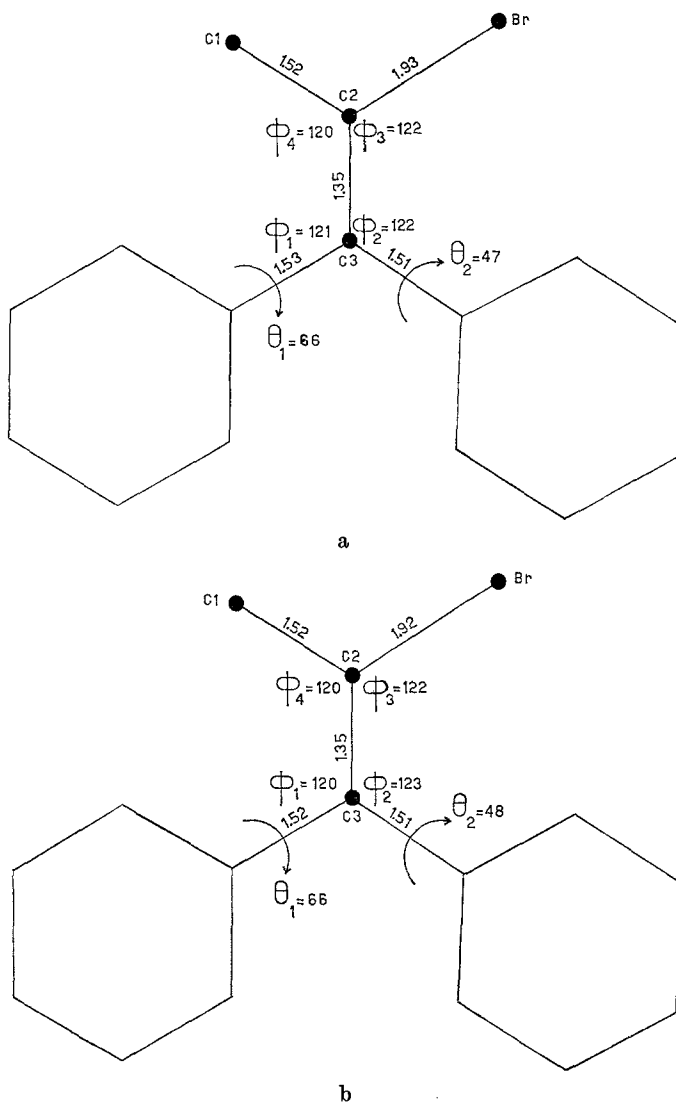
a

b

Fig. 4

Geometries corresponding to the total energy minimum in the reference systems A and B

b) Model Crystal

Two different reference systems for the model molecules in the crystal were considered.

In the first one (A) the necessary geometrical data obtained from experiment were assumed without corrections.

In the second one (B) it was assumed that the C1 atom was shifted to a new *experimental* position suggested by the theoretical results, still in the same plane but at a distance of 1.35 Å from the C3 and 1.52 Å from the C1 atom. As a consequence the C2–C3 bond was rotated by a small angle (0.5°) toward C1.

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Table 1

I. Identification of the interacting molecules:

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Molecule	Position
F	x, y, z
F'	$1 + x, y, z$
F''	$-1 + x, y, z$
P	$x, \frac{1}{2} - y, \frac{1}{2} + z$
Q	$x, \frac{1}{2} - y, -\frac{1}{2} + z$
R	$-x, 1 - y, -z$
S	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
T	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$
U	$-1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
V	$1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$
W	$1 - x, 1 - y, 1 - z$

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II. Intermolecular contacts:

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Atom of Molecule F	with Atom	of Molecule	Distance (Å) model A	model B
H10	H2	P	2.35	2.37
H2	H10	Q	2.35	2.37
H4	H7	R	2.33	2.30
H7	H4	R	2.33	2.30
H2	Br	F'	2.92	2.90
Br	H2	F''	2.92	2.90
H9	H7	F'	2.33	2.33
H7	H9	F''	2.33	2.33
H10	H6	F'	2.33	2.33
H6	H10	F''	2.33	2.33
H9	Br	S	3.13	3.12
Br	H9	T	3.13	3.12
C1	H2	U	3.18	3.15
H2	C1	V	3.18	3.15
C1	H3	U	2.82	2.82
H3	C1	V	2.82	2.82

The two geometries obtained through minimization of the total energy (here-after indicated as crystal model A and B) are shown in Fig. 4A and 4B. The corresponding energies are $E_A = -544.213$ Kcal/mole and $E_B = -544.174$ Kcal/mole.

For these geometries the pairs of interacting atoms in different molecules are shown in Tab. 1 together with the involved distances. The main difference in geometry produced by the packing seems to be a decrease of the ϑ_2 angle from 55° to 47° (A) or 48° (B); the experimental ϑ_2 value is 47°.

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c) Comparison with Experiment

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It must be pointed out that the direct comparison between the *theoretical* structure and the experimental results is not very good.

For example for the geometry of model B, even using the experimentally determined positions of C3 atom, C2–C3 axis, C2, C3, C4, C10 plane, the calculated
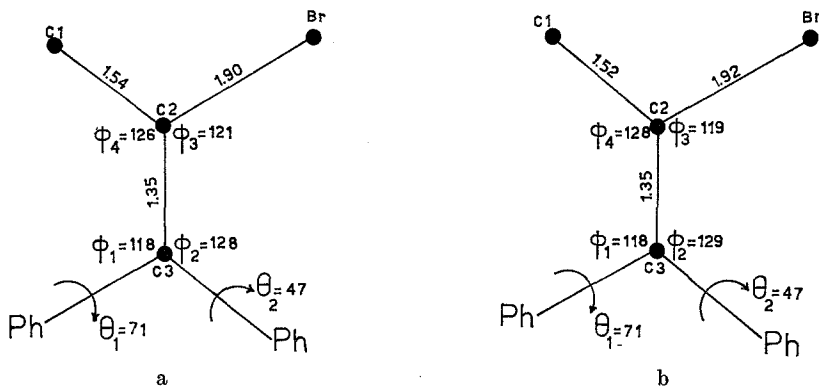
Fig. 5. Corrected experimental geometries. (Unreported angles and distances are the same as in Fig. 1)

reliability index with isotropic thermal factors was $R = 34\%$. This result was slightly improved shifting the molecule as a rigid body in such a way to locate the Br atom in the experimental position: the reliability index was now $R = 29\%$.

These values of the reliability indices should be compared with a value of 16% obtained from the experimental data using isotropic thermal factors and before starting with the least squares refinement procedure. The large discrepancy is easily understood if one thinks that small deviations of one geometrical parameter, for example the value of one of the φ_i's, can produce a sensible modification in the atomic coordinates. Besides, the assumption of regular hexagonal benzene rings seems to be too strong.

Since, owing to the proximity of the Br atom, the position of the C2 atom in the real crystal could have been determined with insufficient accuracy, the experimental findings were corrected shifting in two different ways the C2 atom. This led to the *experimental* situations shown diagrammatically in Fig. 5A and 5B. In both cases we obtained $R = 8.6\%$ (with anisotropic thermal factors).

This suggested that both the experimental and theoretical data point to a value of 1.35 Å for the C2–C3 distance.

We are left with the problem of the choice of A and B. The difference in energy between the two models is as low as 0.039 Kcal/mole and cannot be used to make a decision.

By comparison of Fig. 4A with 5A and 4B with 5B we conclude that model B is the structure in better agreement with experimental and theoretical results.

One may conclude that, at this level of approximation, theoretical considerations are by themselves not sufficient for the refinement of a crystal structure but adequate to suggest some better interpretation of the experimental results. Conversely it is expected that theoretical methods of the kind reported in the present work could be in the future a valuable aid for the solution of the phase problem.

Literature

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