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Molecular Structure of Gaseous Cyclobutane-1,2-dione by Electron Diffraction

Kolbjørn Hagen¹ and Kenneth Hedberg*

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Abstract: The molecular structure of cyclobutane-1,2-dione has been investigated by electron diffraction from the gas. The molecule was found to be planar to within experimental error, in agreement with conclusions from a microwave spectroscopic investigation. The results for some of the more important bond lengths (r_a), bond angles, and root-mean-square amplitudes of vibration (l) with uncertainties estimated at 2σ are: $r(\text{C—H}) = 1.101$ (8) Å, $r(\text{C=O}) = 1.194$ (2) Å, $r(\text{CO—CO}) = 1.575$ (16) Å, $r(\text{CO—CH}_2) = 1.550$ (14) Å, $\angle\text{CO—CO=O} = 135.9$ (10)°, $\angle\text{CO—CO—CH}_2 = 89.5$ (2)°, $\angle\text{C—C—H} = 114.4$ (5)°, $l(\text{C—H}) = 0.0849$ (113) Å, $l(\text{C=O}) = 0.0369$ (19) Å, $l(\text{CO—CO}) = 0.0568$ (30) Å. The structure is discussed.

The gas-phase structure of molecules with conjugated bonds has been an area of interest in this laboratory for many years. Among such molecules are those with adjacent carbonyl groups, such as the oxalyl halides and biacetyl, which in principle may exist in more than one conformation arising from internal rotation about the conjugated carbon-carbon bond. In the cases of oxalyl chloride² and oxalyl bromide³ both a lower energy anti form and a higher energy gauche form are present in substantial amounts in room-temperature samples of the vapors, but in biacetyl⁴ only the anti form is found even at temperatures of several hundred degrees.

In a small-ring compound such as cyclobutane-1,2-dione (CBD, Figure 1) the carbonyl groups are necessarily constrained to a syn, or near syn, conformation. The possible structural effects of this otherwise unpreferred arrangement interested us and we decided to carry out an electron-diffraction investigation of the molecule. Although the three nonequivalent carbon-carbon bonds could only be slightly different in length, we were optimistic about obtaining accurate values from them: three rotational constants together with proof that the heavy-atom part of the CBD molecule is planar were available from microwave spectroscopy⁵ and could be incorporated into the structure refinements. Such joint refinements generally remove uncertainties attached to the resolution of nearly equal distances when only electron-diffraction data are available.

Experimental Section

The sample of CBD was prepared by Professor J. M. Conia as earlier described.⁶

Diffraction photographs were made in the Orgeon State apparatus at a nozzle-tip temperature of 100 °C under the following conditions: sector shape, r^2 ; plates, 8×10 and 5×7 in Kodak projector slide, medium contrast; development, 10 min in D-19 diluted 1:1; ambient apparatus pressure during exposure, 4.0×10^{-6} to 1.8×10^{-5} torr; exposure times, 1–8 min; beam currents, 0.40–0.47 μA; nozzle-to-plate distances, 74.977, 29.986, and 12.040 cm; electron wavelengths, 0.05743–0.05747 Å; wavelength standard, CO₂ with $r_a(\text{C=O}) = 1.1646$ Å and $r_a(\text{O—O}) = 2.3244$ Å.

Three plates from each of the three camera distances were selected for analysis. The procedures for obtaining the leveled total intensities ($s^4 I_T(s)$) and the molecular intensities ($s I_m(s)$) have been described.^{7,8}

The ranges of the data were $2.00 \leq s \leq 12.50$ Å⁻¹ (long camera distance), $8.00 \leq s \leq 30.75$ Å⁻¹ (intermediate distance), and $25.00 \leq s \leq 45.00$ Å⁻¹ (short distance). Figure 2 shows curves of the leveled total intensities and final calculated backgrounds; these data are available as supplementary material. Averages of the molecular intensities $s I_m(s)$ from each of the camera distances are shown in Figure 3.

Calculations of intensity and radial distribution (RD) curves were carried out according to the equations

$$s I_m(s) = k \sum_{i \neq j} (A_i(s) A_j(s) r_{ij}^{-1} V_{ij}(s) \cos |\Delta \eta_{ij}(s)| \sin [s(r_{ij} - \kappa s^2)]) \quad (1)$$

and

$$r D(r) = \frac{2}{\pi} \Delta s \sum_{s=0}^{\infty} I'(s) \exp(-B s^2) \sin r s \quad (2)$$

with $V_{ij} = \exp(-l_{ij}^2 s^2 / 2)$ and $I' = s I_m(s) Z_C Z_O A_C^{-1} A_O^{-1}$. Electron scattering amplitudes $F_i = A_i / s^2$ and phases η_i were obtained⁷ from tables.⁹ Values of the anharmonicity constants κ were estimated from the diatomic molecule approximation¹⁰ to be 12.6×10^{-6} , 0.59×10^{-6} , and 1.45×10^{-6} Å⁻³ for the C—H, C=O, and C—C bonds, respectively; values for the nonbond distances were assumed to be zero. Experimental RD curves were calculated from composites of the average intensity curves, averaged in the overlap regions, using data from theoretical intensity curves for the unobserved region $s < 2.00$ Å⁻¹. The final RD curve is shown in Figure 4.

Structure Analysis

The positions of the peaks of the experimental RD curve led in a straightforward way to a trial structure consistent with that depicted in Figure 1. Least-squares refinements¹¹ of the structure were done by fitting a single theoretical intensity curve (eq 1) to the three average experimental curves of Figure 3, and, simultaneously, the three corresponding calculated rotational constants to the experimental ones. Because of the effect of vibrational averaging, the r_a distances appropriate to eq 1 are inappropriate for rotational constants. We defined our models in terms of the geometrically consistent $r_a^0 = r_z$ set of distances which were used to calculate rotational constants $B_z = 505379 \text{ MHz} \cdot \text{u} \cdot \text{Å}^2 / I_z$ related to the observed B_0 by

$$B_z = B_0 + \frac{1}{2} \sum_s \alpha_s \bar{\alpha}_s \quad (3)$$

The r_a distances for the temperature of interest were generated from the r_a^0 set of the model according to¹²

$$r_a^T = r_a^0 + (\frac{3}{2}) a_3 [(I^T)^{-1} - (I^0)^{-1}] + \delta r^T + K^0 - (I^T)^{-1} / r_a^0 \quad (4)$$

The Morse function anharmonicity constants a_3 were given the diatomic molecule values¹³ for bonds and otherwise assumed to

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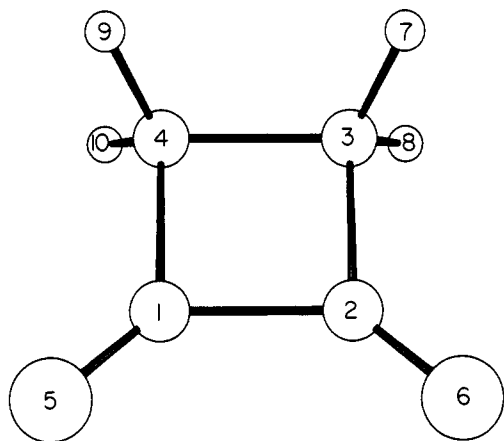


Figure 1. Diagram of cyclobutane-1,2-dione with atomic numbering.

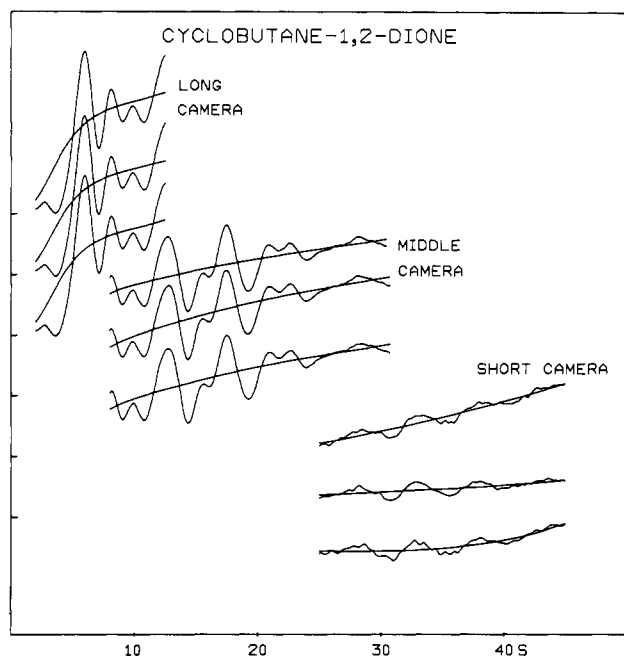


Figure 2. Intensity curves, $s^4 I_T$, shown superimposed on the final backgrounds. The intensity curves are magnified five times in order to show better the molecular part of the scattering.

be zero. Values for centrifugal distortion, perpendicular amplitudes, and some of the mean-square amplitudes (δr , K , and I^2 , respectively), as well as the α^{har} (eq 3), were calculated from an assumed harmonic force field. The constants of this force field were given values consistent with those for bond stretches and angle bends in similar molecules. The vibrational spectrum of CBD has not been reported, but the frequencies calculated from our assumed force field appear to be reasonable. The C_{2v} symmetry coordinates, force constants, and calculated frequencies are available in the supplementary material.

Our model of CBD, assumed to have C_{2v} symmetry, was defined by the geometrical parameters $r(\text{C-H})$, $r(\text{C=O})$, $r(\text{C}_1\text{-C}_2)$, $r(\text{C}_2\text{-C}_3)$, $\angle \text{C}_1\text{C}_2\text{C}_3$, $\angle \text{C}_1\text{C}_2\text{O}_6$, and $\angle \text{CCH}$, and by the vibrational parameters (I) evident from Table I. (The assumption of C_{2v} symmetry is consistent with the microwave results. Also, it was found to be consistent with the diffraction data alone: values obtained for the torsion angle $\phi = \angle \text{OCCO}$ in test refinements differed insignificantly from zero.) All distances were included in the refinements except vicinal $\text{H}\cdots\text{H}$.

The final results are given in Table I and the correlation matrix in Table II. Theoretical intensity and radial distribution curves are shown in Figures 3 and 4. The final model clearly provides an excellent fit to the diffraction data. The fit to the microwave data is also very good: the observed values⁵ (in MHz) $A_0 = 5329.1$,

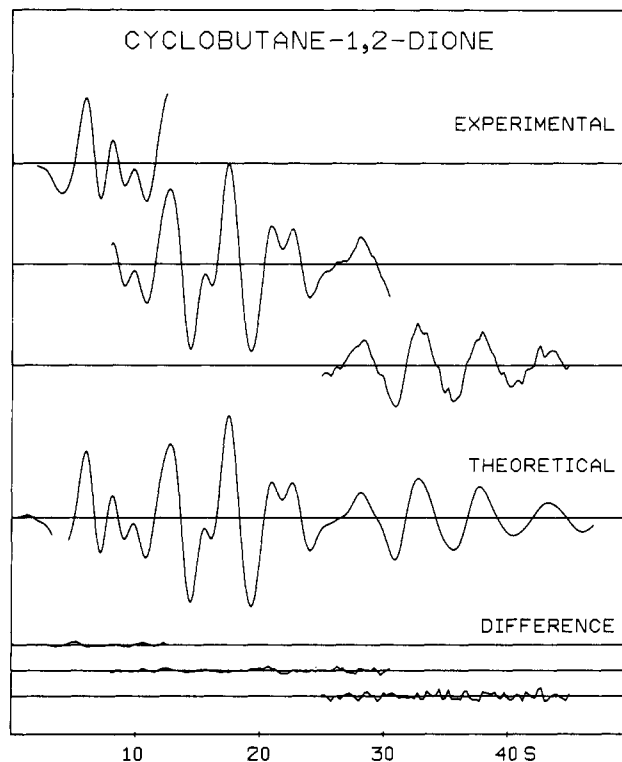


Figure 3. Intensity curves. The experimental curves are averages of $s^4 I_m(s)$ for each camera distance. The theoretical curve is for the model in Table II. The difference curves are experimental minus theoretical.

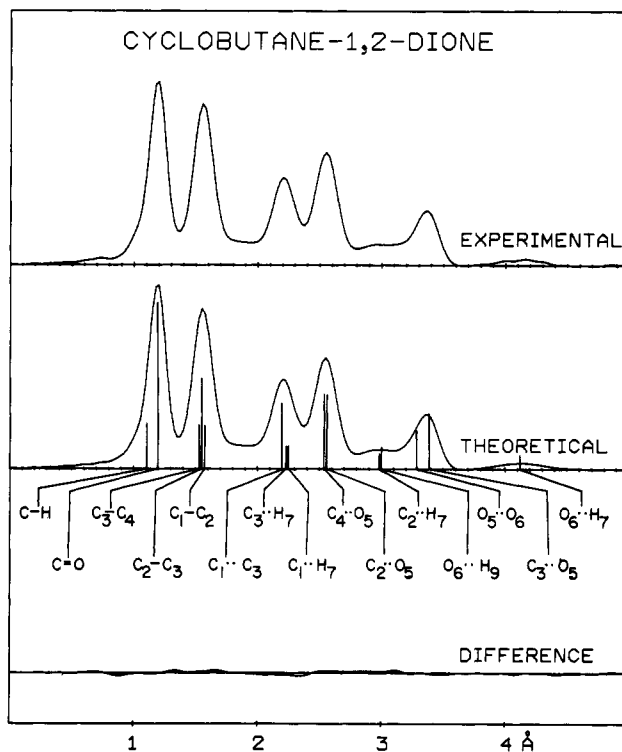


Figure 4. Radial distribution curves. The experimental curves are calculated from composites of the molecular intensities shown in Figure 3. The theoretical curve corresponds to the model of Table II. The convergence factor coefficient B was 0.0012 \AA^2 . The vertical lines correspond to the distances in Table II; their lengths are proportional to the weights of the terms. The difference curve is experimental minus theoretical.

$B_0 = 4050.5$, $C_0 = 2371.1$ converted to $A_z = 5332.8$, $B_z = 4052.2$, $C_z = 2370.8$ are each reproduced to within 0.3 MHz. It is pleasing that refinements carried out by using only the diffraction data

Table I. Structure Results for Cyclobutane-1,2-dione^a

distance type or angle	$r_{\alpha}^a; L$	r_g^b	r_a^b	l	l_{calcd}^c
C-H ^d	1.096 (8)	1.108	1.101	0.085 (11)	0.079
C=O ^d	1.191 (2)	1.195	1.194	0.037 (2)	0.037
C ₁ -C ₂ ^d	1.574 (16)	1.577	1.575	0.057	0.050
C ₂ -C ₃ ^d	1.549 (14)	1.553	1.550	0.058	0.051
C ₃ -C ₄ ^d	1.544 (14)	1.549	1.547	0.054	0.051
C ₁ -C ₃	2.198 (3)	2.200	2.199	0.060 (5)	0.060
C ₂ -O ₅	2.566 (7)	2.569	2.567	0.066	0.062
C ₄ -O ₆	2.532 (4)	2.534	2.532	0.068	0.064
C ₃ -O ₅	3.389 (4)	3.390	3.389	0.066 (6)	0.063
O ₅ -O ₆	3.285 (13)	3.292	3.290	0.090 (15)	0.090
C ₁ -H ₇	2.236 (11)	2.247	2.243	0.096	0.114
C ₃ -H ₇	2.232 (18)	2.245	2.241	0.095	0.113
C ₂ -H ₇	2.976 (12)	2.984	2.977	0.153	0.151
O ₆ -H ₈	2.999 (6)	3.007	2.999	0.157	0.156
O ₅ -H ₇	4.128 (13)	4.133	4.125	0.178 (79)	0.200
H ₇ -H ₈	1.775 (21)	1.796	1.783	0.152	0.152
<C-C>	1.555 (1)	1.558	1.556		
$\angle C_1C_2C_3$ ^d	89.5 (2)				
$\angle C_1C_2O_5$ ^d	135.9 (10)				
$\angle CCH$ ^d	114.4 (5)				
$\angle HCH$	108.2 (17)				
R^e	0.0725				

^a Distances and amplitudes in angstroms, angles in degrees. Quantities in parentheses are estimated 2σ and those in brackets were refined as a group. ^b Uncertainties on r_a and r_g values are the same as for r_{α} . ^c Calculated from assumed harmonic force field. See text. ^d Used to define the geometry. See text. ^e $R = [\sum w_i \Delta_i^2 / \sum w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

gave results insignificantly different from those in the tables.

Discussion

There are a number of interesting features of the CBD structure. The weighted average C-C bond length ($r_g = 1.558$ (2) Å) is about 0.02 Å longer than C-C single bonds in aliphatic chains. A similar circumstance occurs in the case of cyclobutane itself ($r_g = 1.555$ (3) Å¹⁴), where it was suggested^{14c} that the bond lengthening arose from cross-ring repulsions: because the geminal carbon atoms are closer in a four-member ring than in open chains, the nonbond repulsions should be greater. The same argument should apply to CBD.

The differences between the lengths of the three types of ring bonds in CBD are not measured so accurately as is the average distance, but it is apparent that the bond between the carbonyl groups is longer than the others. We attribute this greater length to repulsion between residual positive charges on the carbon atoms arising from the polar carbonyl bonds: charges of about +0.4 electron unit are calculated from the value 2.4 D estimated for the carbonyl bond moment. It is worth noting that the bonds between adjacent carbonyl groups in many other molecules are also longer than might have been expected. For example, the anti forms of oxalyl chloride, oxalyl bromide, oxalic acid, and biacetyl are found to be the most stable of the possible several conformers, presumably because of conjugation stabilization which should shorten the conjugated bond. Nevertheless, the measured distances in these compounds ($r = 1.534$ (5) Å², 1.546 (8) Å³, 1.548 (4) Å¹⁵, and 1.530 (14) Å^{4a}, respectively) are about the same as carbon-carbon bonds in saturated chains. The polarity effects mentioned above should also operate for the other ring bonds. Thus, atoms C₃ and C₄ are each expected to obtain about -0.1 e charge from the C-H bond, leading to repulsion along C₃-C₄ and, in view of the positive charges on the other carbon atoms, to attraction along C₁-C₄. Unfortunately, the magnitudes of the corresponding distance changes are expected to be much less than

Table II. Correlation Matrix (×100) for Cyclobutane-1,2-dione

σ_{LS}^a	$r(C-H)$	$r(C=O)$	$r(C_1-C_2)$	$r(C_2-C_3)$	$r(C_3-C_4)$	$\angle C_1C_2O$	$\angle C_1C_2C_3$	$\angle CCH$	$\angle(C-H)$	$\angle(C=O)$	$\angle(C_1-C_2)$	$\angle(C_2O_5)$	$\angle(C_1C_3)$	$\angle(C_3O_6)$	$\angle(O_5O_6)$
0.26	100	0.03	0.58	0.48	0.50	35.0	5.4	18.2	0.38	0.04	0.07	0.09	0.14	0.21	0.53
		-2	36	-47	20	-40	-11	17	-2	-6	-36	-31	-15	-21	-6
		100	8	-20	28	-17	35	-4	-47	-15	-3	-5	-2	-11	-15
			100	-98	87	-99	-54	26	-1	-1	-75	-55	-19	-48	-30
				100	-93	99	39	-34	7	3	73	56	22	49	31
					100	-93	4	8	-10	-1	73	-48	-20	-51	-35
						100	41	-28	6	2	47	56	21	50	32
							100	-9	-15	-3	21	23	-8	11	-1
								100	2	-1	-21	-20	-13	-14	-3
									41	5	5	8	6	8	7
									100	26	30	15	14	14	8
										53	18	18	42	42	23
										100	36	34	36	36	18
											100	100	100	100	46
															100

^a Standard deviations (×100) from least squares. Distances and amplitudes in angstroms, angles in degrees.

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that for C₁-C₂ so that our measurements with their large uncertainties provide no experimental evidence on the point. Some supporting evidence is available in the results of X-ray diffraction investigation of [4.4.2]propella-3,8-diene-11,12-dione,¹⁵ a molecule with a CBD subunit, and *trans*-3,4-di-*tert*-butylcyclobutane-1,2-dione¹⁷. The first of these has distances of 1.551 (3) Å, 1.534 (3) Å, and 1.572 (3) Å for the bonds corresponding to C₁-C₂, C₁-C₄, and C₃-C₄ in CBD; the second has distances of 1.560 (3) Å, 1.527 (2) Å, and 1.560 (3) Å. Thus the C₁-C₂ type distance is in each case longer than normal and the C₁-C₄ type smaller than its neighbors.

The C=O bond length in CBD ($r_g = 1.194$ (2) Å) is about 0.02 Å shorter than those found in aliphatic ketones. We attribute the shortening to diminished nonbond repulsions involving the C=O and adjacent bonds, and the oxygen atom and geminal carbons. Since the proximity of the opposing bonds and atoms depends most importantly on the CCC bond angle at the base of the carbonyl group, the C=O bond length should decrease as this angle decreases. This is observed to be the case: In CBD and

in the similar propelladienedione and *tert*-butyl compounds mentioned above the C=O bond lengths are respectively 1.194 (2) Å, 1.192 (2) Å, and 1.191 (2) Å, (C=O base angles ~90°); and in 2-cyclopentane-1,4-dione,¹⁸ and *p*-benzoquinone¹⁹ (C=O base angles respectively 108.2 (4)° and 118.1 (3)°) the C=O bond lengths are 1.208 (2) Å and 1.225 (2) Å.

The measured amplitudes of vibration are generally in good agreement with those calculated from our assumed force field. The agreement is poorest for the ring bonds. However, we attribute no special significance to this fact because the values of these amplitudes are highly correlated with the values of the distances which bear large uncertainties.

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Supplementary Material Available: Tables of total intensities, final backgrounds, average molecular intensities, symmetry coordinates, force constants, and calculated frequencies (11 pages). Ordering information is given on any current masthead page.

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Conformational Studies of Dihydrotetraphenylmethanes. 1. X-ray Crystallographic and Solution ¹H NMR Studies of *trans*-1,4-Dihydro-4-tritylbiphenyl and Its 4'-Bromo Derivative: Boat-Boat Inversion in a Congested Cyclohexa-1,4-diene

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Contribution from the Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD, England, and the Department of Chemistry, Bedford College University of London, Regent's Park, London, NW1 4NS, Enland. Received January 9, 1981

Abstract: Single-crystal X-ray diffraction measurements on 1,4-dihydro-4-tritylbiphenyl and on two crystal modifications of its 4'-bromo derivative reveal that the three molecular structures are remarkably similar, the only variation being the sense of puckering of the cyclohexa-1,4-diene ring. Crystals of 1,4-dihydro-4-tritylbiphenyl are orthorhombic, space group *Pnam*, *Z* = 4, lattice parameters *a* = 10.083 (1), *b* = 12.128 (2), *c* = 18.247 (5) Å; 1201 independent reflections gave a final *R* of 0.050. The orthorhombic form of 4'-bromo-1,4-dihydro-4-tritylbiphenyl has space group *Pnam*, *Z* = 4, *a* = 13.012 (2), *b* = 17.264 (3), *c* = 10.431 (1) Å; 894 independent reflections gave a final *R* of 0.046. In contrast, the monoclinic form has space group *Pc*, *Z* = 2, *a* = 9.011 (1), *b* = 16.187 (3), *c* = 8.463 (2) Å, $\beta = 108.98$ (1)°; 1205 independent reflections gave a final *R* of 0.041. Comparison of the three structures suggests that the cyclohexa-1,4-diene ring in 1,4-dihydro-4-tritylbiphenyls exists in either a shallow potential well with a single minimum corresponding to an essentially planar cyclohexadiene geometry or a double-minimum potential well in which there is rapid boat inversion. There is no evidence for the highly puckered boat conformation previously suggested. A reassessment of the ¹H NMR data for these compounds also supports this view. The close similarity of the molecules analyzed provides a rare opportunity for the evaluation of the relative importance of intramolecular interactions and intermolecular or "packing" forces on the solid-state geometries of these molecules. It is concluded that while the steric requirements of the dihydrotetraphenylmethane molecule prescribe an essentially planar cyclohexa-1,4-diene geometry, the exact conformation of the ring is controlled by crystal packing requirements.

Introduction

Long-range ¹H NMR coupling constants provide a convenient probe into the solution conformations of organic molecules.¹ In principle, for a derivative of cyclohexa-1,4-diene (1),² an analysis of vicinal couplings could indicate the overall ring conformation.

However, such couplings are generally small when saturated carbon centers are involved, and the effect of large variations in ring geometry may be reflected by only slight changes in the magnitudes of such short-range interactions.³ Allylic couplings,⁴

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