charge when attached to boron; however, it is more positive relative to hydrogen in borazine.

In their early treatment of borazine Roothaan and Mulliken assumed that the Hückel Coulomb integral is proportional to the electronegativity of the atom.[3] This led them to conclude that for borazine, α_N was the same amount greater than α_C in benzene as α_B was less. The SCF diagonal $F_{p\pi p\pi}$ elements of the present work which are the analogs of the Hückel α's are found to approximate Roothaan and Mulliken's proposal.

From the net charges and π charge densities given in Table IV we may calculate the core charge seen by the π electron. In borazine the values are +0.798 for boron and +1.293 for nitrogen. These are closely (but not exactly) related to the core charges, ζ_ν, which are used to compute the diagonal elements for a Pariser–Parr–Pople-type of calculation ($\zeta_\nu = \zeta_J - Q_J$ of eq 1). The problems associated with the choice of the P–P–P core charge for borazines have been recognized in the past but never thoroughly resolved. Davies[7] showed that, for the calculation of electronic spectra, it is not necessary to assign the polarity of the core, since this cancels out when energy differences are computed. Unfortunately, his method cannot be extended to the calculation of ionization potentials and other interesting properties. A somewhat different approach was adopted by Chalvet, Daudel, and Kaufman,[6] who employed two different sets of core charges, which bracket those calculated here. Future Pariser–Parr–Pople calculations on borazine-like molecules might be improved by the use of +0.8 and +1.2 core charges for boron and nitrogen, respectively.[54]

Acknowledgment. The authors are grateful for the generous allotment of computer time by the Vogelback Computing Center of Northwestern University. We also wish to acknowledge a conversation with Professor J. A. Pople in which he described the CNDO method before published accounts were available.

(54) Occasionally the core charge is identified as the number of electrons donated to the π system by an atom. This terminology is to be discouraged because it presupposes a nonpolar σ core, which will generally not be the case when heteroatoms are present.

The Crystal Structures of Two Novel Polycyclic Products, $C_{26}H_{26}O_2$ and $C_{24}H_{10}$, from the Photolysis of *anti*-[2.2]Paracyclonaphthane

Albert V. Fratini[1]

Contribution from the Naval Research Laboratory, Washington, D. C. 20390.
Received September 11, 1967

Abstract: X-Ray crystallographic techniques employing the symbolic addition procedure for phase determination have been used to elucidate the structures of two polycyclic products from the photolysis of *anti*-[2.2]paracyclonaphthane, a dibenzodimethoxy compound (II) and dibenzoequinene (IV), a centrosymmetrical hydrocarbon. Both molecules crystallize in space group $P2_1/n$ with cell parameters $a = 7.88 \pm 0.02$ Å, $b = 16.17 \pm 0.02$ Å, $c = 14.92 \pm 0.02$ Å, $\beta = 91°57' \pm 15'$ for II, and $a = 10.14 \pm 0.02$ Å, $b = 7.90 \pm 0.02$ Å, $c = 10.07 \pm 0.02$ Å, $\beta = 101°30' \pm 15'$ for IV. The six-membered rings which form *via* the internal Diels–Alder reaction of the inner rings of naphthalene system all have the boat conformation. The cyclobutane ring in IV is highly puckered with a dihedral angle of 124.5° and an average C–C bond length of 1.576 Å.

In the course of their investigations of the reactions of singlet oxygen with strained aromatic systems, Wasserman and Keehn[2] have found that the photosensitized autoxidation of *anti*-[2.2]paracyclonaphthane leads to two novel polycyclic products, a dibenzodimethoxy polycyclic (II) and the centrosymmetrical hydrocarbon, dibenzoequinene (IV). The major product of the photoxidation reaction is II while IV is observed as a minor product. Recently, however, IV has been found to be the main product in the purely photochemical reaction in the absence of oxygen.[2b]

It is believed that the photoxidation reaction proceeds in several stages. The first step involves the addition of singlet oxygen to the naphthalene system to form a transannular peroxide followed by a second-stage internal Diels–Alder reaction. Solvolysis in methanol leads to II. Dibenzoequinene (IV) appears to form by a light-induced intramolecular cyclization possibly through the intermediate III. Naphthalene normally does not add oxygen in the manner described above; however, the strain associated with the out-of-plane distortions of the naphthalene rings is thought to impart greater reactivity to the dienoid system. Such ring deformations have been demonstrated in similar systems. For example, Gantzel and Trueblood[3] have reported the X-ray structure determination of [3.3]-paracyclophane in which the aromatic rings are deformed slightly into a symmetrical boat form, the bending being about 6° at each end. Out-of-plane

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(1) National Academy of Sciences–National Research Council Postdoctoral Resident Research Associate, 1965–1967. Address inquires to the Chemistry Department, University of Dayton, Dayton, Ohio.

(2) (a) H. H. Wasserman and P. M. Keehn, *J. Am. Chem. Soc.*, **88**, 4522 (1966); (b) *ibid.*, **89**, 2770 (1967).

(3) P. K. Gantzel and K. N. Trueblood, *Acta Cryst.*, **18**, 958 (1965).

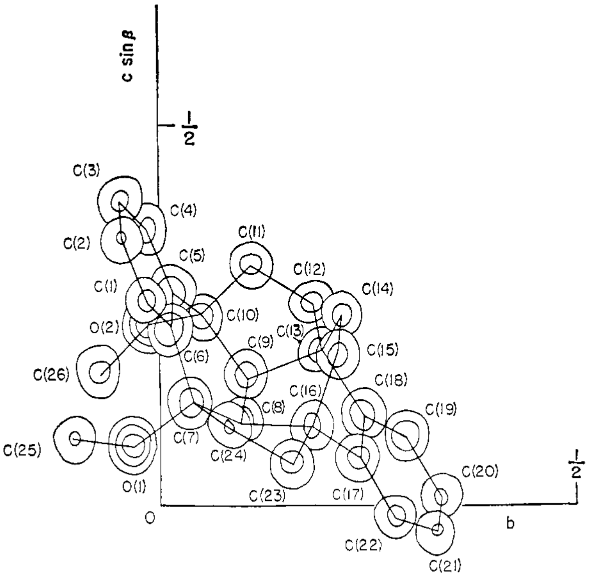
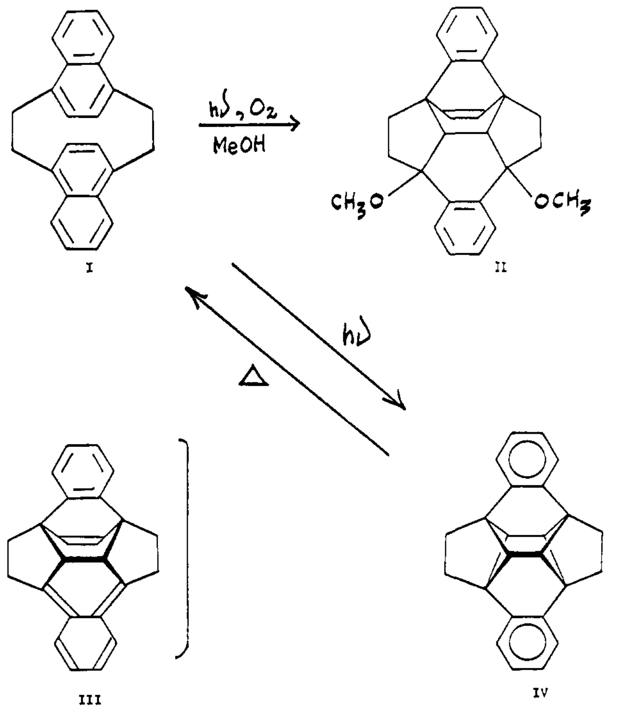


Figure 1. Sections of the three-dimensional electron density map of the dibenzodimethoxy compound projected along (100). The contours start at 2.5 e/Å³ and are spaced at intervals of 2.5 e/Å³.

distortions of the aromatic rings have been found in [2.2]paracyclophane and related compounds.[4]



Structures II and IV were consistent with all chemical and physical data (nmr, ir, mass spectrometry). The X-ray structure determination was carried out in order to confirm their molecular configurations and determine the values of their structural parameters. Furthermore, the results of this work demonstrate the utility of X-ray crystallographic techniques in the identification of the products of complicated photochemical reactions and the elucidation of their structures.[5]

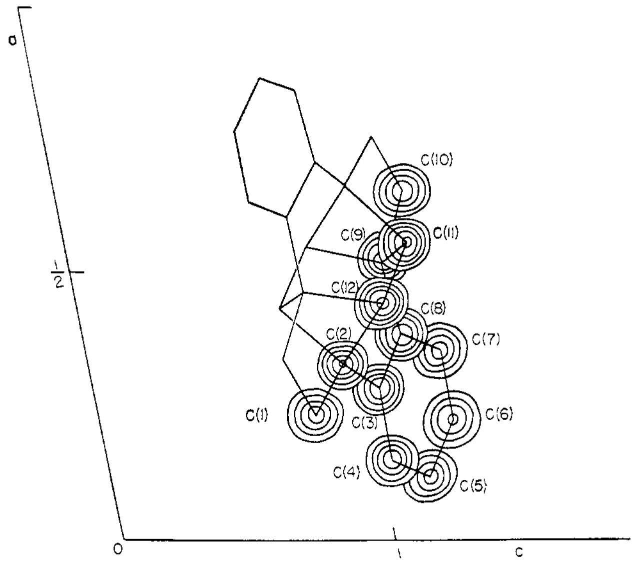


Figure 2. Sections of the three-dimensional electron density map of dibenzoquinene projected along (010). The contours start at 2.0 e/Å³ and are spaced at intervals of 2.0 e/Å³. The contours are drawn for only half the atoms since the molecule is centrosymmetric.

Experimental Section

Crystals of both materials were supplied by Professor Harry H. Wasserman of Yale University. The crystals were colorless, II

Table I. Experimental Data for II and IV

	Dibenzodimethoxy compd (II)	Dibenzoequinene (IV)
a, Å	7.88 ± 0.02	10.14 ± 0.02
b, Å	16.17 ± 0.02	7.90 ± 0.02
c, Å	14.92 ± 0.02	10.07 ± 0.02
β	91° 57′ ± 15′	101° 30′ ± 15′
$\rho_{\text{X-ray}}$, g cm^{-3}	1.204	1.295
Space group	$P2_1/n$	$P2_1/n$
Total obsd reflections	1967	1196
No. of molecules/unit cell	4	2
$\langle \lvert E \rvert \rangle$	0.746	0.785
$\langle \lvert E^2 - 1 \rvert \rangle$	1.00	0.972
Crystal size, mm	0.5 × 0.1 × 0.1	~0.15 × 0.15 × 0.15

Table II. Approximate Hydrogen Atom Positions for II and IV

Atom	x	y	z	Atom	x	y	z
			Dibenzodimethoxy Compound (II)				
H(1)	1.466	−0.016	0.230	H(19)	0.583	0.303	0.103
H(2)	1.503	−0.081	0.386	H(20)	0.651	0.378	−0.018
H(3)	1.215	−0.056	0.461	H(21)	0.891	0.351	−0.103
H(4)	0.950	−0.011	0.413	H(22)	1.175	0.296	−0.033
H(8)	1.053	0.071	0.046	H(23,1)	1.293	0.146	−0.013
H(9)	0.786	0.095	0.136	H(23,2)	1.416	0.213	0.066
H(11,1)	0.730	0.070	0.350	H(25,1)	1.260	−0.130	0.166
H(11,2)	0.883	0.121	0.366	H(25,2)	1.215	−0.150	0.053
H(12,1)	0.636	0.166	0.241	H(25,3)	1.421	−0.095	0.083
H(12,2)	0.768	0.238	0.315	H(26,1)	0.935	−0.103	0.203
H(14)	1.075	0.243	0.313	H(26,2)	0.703	−0.111	0.166
H(15)	1.328	0.228	0.213	H(26,3)	0.850	−0.053	0.098
			Dibenzoequinene (IV)				
H(1,1)	0.181	1.100	0.326	H(7)	0.433	0.533	0.686
H(1,2)	0.178	1.228	0.470	H(10,1)	0.673	0.700	0.736
H(4)	0.080	0.866	0.468	H(10,2)	0.658	0.555	0.610
H(5)	0.023	0.651	0.583	H(11)	0.588	1.025	0.720
H(6)	0.203	0.416	0.683	H(12)	0.416	1.208	0.618

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(4) D. A. Bekoe and K. N. Trueblood, Meeting of the American Crystallographic Association, Bozeman, Mont., 1964.

(5) O. Yonemitzu, B. Witkop, and I. L. Karle, *J. Am. Chem. Soc.*, 89, 1039 (1967).

Table III. Fractional Coordinates and Anisotropic Thermal Parameters ($\beta_{ij} \times 10^4$) for the Dibenzodimethoxy Compound[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1.3693	−0.0180	0.2747	86	34	36	11	−8	−5
C(2)	1.3764	−0.0490	0.3606	168	37	32	19	−14	1
C(3)	1.2299	−0.0513	0.4075	202	32	24	19	−5	6
C(4)	1.0774	−0.0179	0.3718	155	25	37	20	1	4
C(5)	1.0714	0.0149	0.2858	55	17	20	0	5	−4
C(6)	1.2153	0.0134	0.2358	65	17	29	4	1	−2
C(7)	1.2146	0.0377	0.1368	83	27	18	7	14	−5
C(8)	1.0699	0.0967	0.1109	56	21	11	−7	10	0
C(9)	0.9166	0.1029	0.1680	91	18	16	−2	9	2
C(10)	0.9057	0.0490	0.2522	34	21	25	0	20	−4
C(11)	0.8166	0.1077	0.3211	125	29	22	3	41	1
C(12)	0.7542	0.1845	0.2696	95	28	34	4	19	3
C(13)	0.8984	0.1944	0.2031	80	18	27	6	−8	−4
C(14)	1.0644	0.2185	0.2505	91	20	25	−4	3	0
C(15)	1.1991	0.2141	0.1994	141	22	29	−16	−6	2
C(16)	1.1585	0.1836	0.1044	76	21	22	−14	14	−2
C(17)	1.0221	0.2402	0.0657	110	23	20	−16	10	1
C(18)	0.8806	0.2472	0.1191	91	19	27	−7	17	−3
C(19)	0.7407	0.2936	0.0937	152	19	49	5	−27	3
C(20)	0.7446	0.3365	0.0110	206	26	42	13	−4	4
C(21)	0.8807	0.3282	−0.0421	281	31	30	−8	−33	8
C(22)	1.0248	0.2822	−0.0169	167	24	29	−12	5	1
C(23)	1.3174	0.1607	0.0560	87	37	28	5	25	1
C(24)	1.3815	0.0817	0.1054	48	42	41	−7	26	−6
C(25)	1.2851	−0.1060	0.0938	166	35	51	29	−21	−11
C(26)	0.8237	−0.0766	0.1743	140	32	48	15	22	15
O(1)	1.1774	−0.0354	0.0807	94	21	33	10	3	−9
O(2)	0.7803	−0.0174	0.2402	93	24	32	−10	19	1
Standard error									
C	0.0012	0.0004	0.0006	22	3	5	6	9	3
O	0.0007	0.0003	0.0003	14	2	3	4	5	2

[a] The thermal parameters are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}kh + 2\beta_{13}hl + 2\beta_{33}kl)]$.

crystallizing in the form of needles elongated along the *a* axis and IV approximating irregular polyhedra with many well-defined faces. Cell dimensions were obtained from precession photographs, whereas intensity data were collected from multiple film, equiinclination Weissenberg photographs with filtered copper radiation. Layers 0*kl* through 5*kl* and *hk*0 were recorded for II, and layers *h*0*l* through *h*5*l* for IV. The intensities were estimated visually by comparison with a calibrated film strip and corrected for Lorentz and polarization factors and spot size. No adsorption corrections were applied. The space group for each crystal was determined unambiguously from the systematic absences. The statistical averages for the normalized structure factor magnitudes, $\langle |E| \rangle$ and $\langle |E^2 - 1| \rangle$, were consistent with centrosymmetric space groups. The pertinent experimental data for both crystals are shown in Table I.

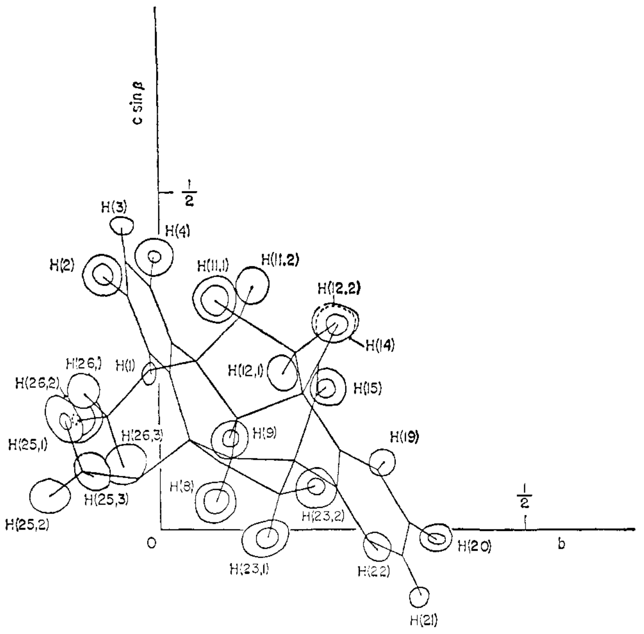

Figure 3. Sections of the difference map of the dibenzodimethoxy compound projected along (100). The contours start at 0.25 e/Å^3 and are spaced at intervals of 0.25 e/Å^3.

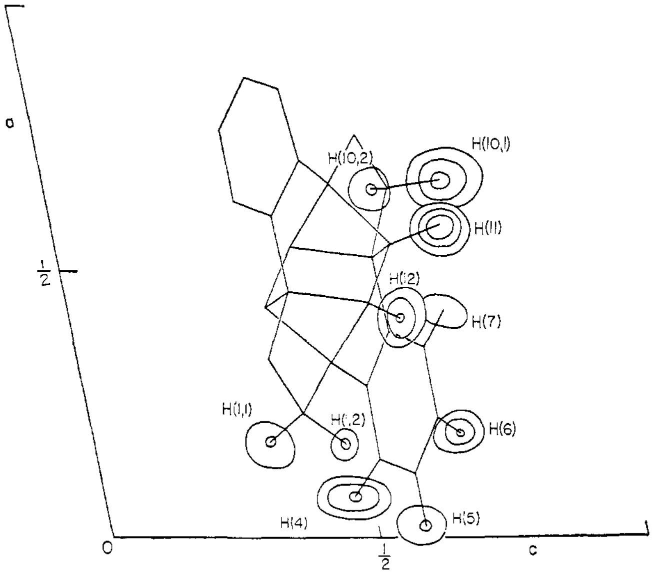

Figure 4. Sections of the difference map of dibenzoequinene projected along (010). The contours start at 0.25 e/Å^3 and are spaced at intervals of 0.25 e/Å^3.

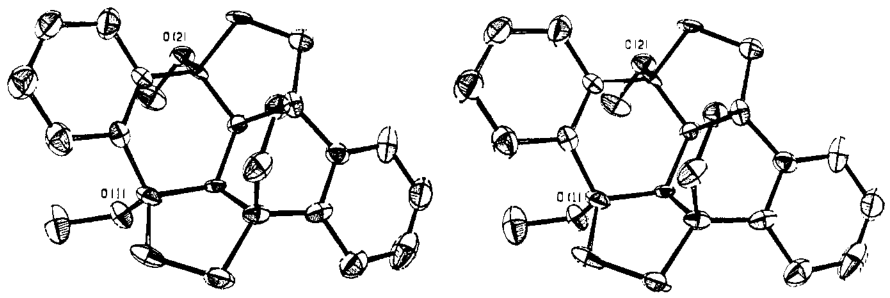

Figure 5. Stereoscopic diagram for the dibenzodimethoxy compound.

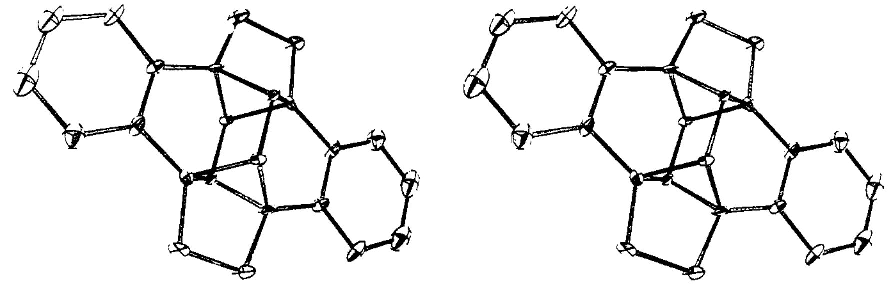

Figure 6. Stereoscopic diagram for dibenzoequinene. The drawing was made by a computer program prepared by C. K. Johnson, OR TEP, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

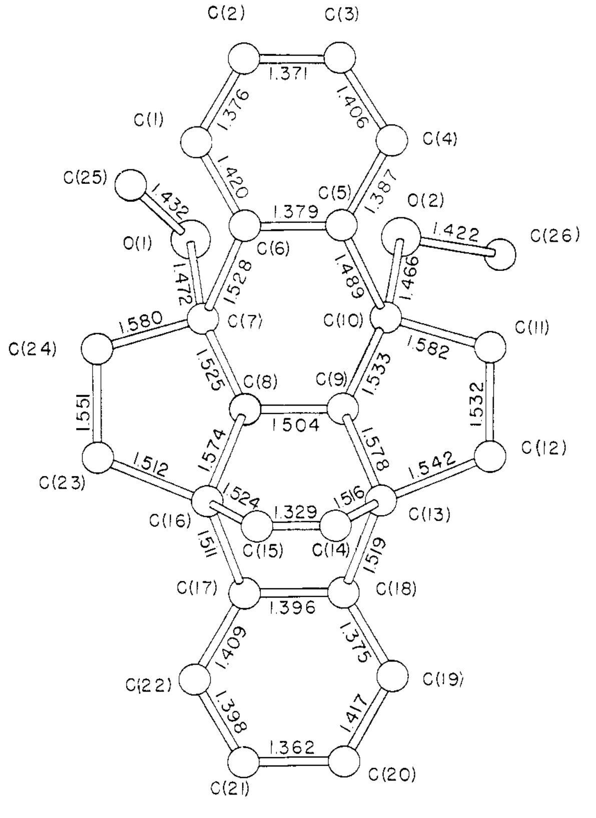

Figure 7. Bond distances for the dibenzodimethoxy compound.

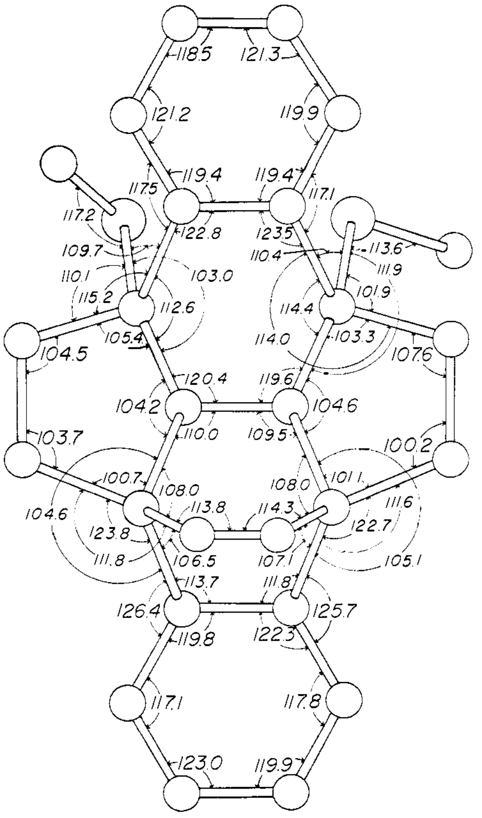

Figure 8. Bond angles for the dibenzodimethoxy compound.

Structure Analysis

The symbolic addition procedure for determining phases directly from the structure factor magnitudes was used.[6] In each compound the most probable set of signs proved to be the correct set. *E* maps computed with 287 reflections having large $|E|$ values for II and 274 reflections for IV clearly showed all atoms in the unit cell. The density of dibenzoequinene indicated that two molecules were contained in the unit cell, which required the molecule to possess a center of symmetry in this space group. Hence half a molecule comprised the asymmetric unit. The final electron density maps for II and IV are illustrated in Figures 1 and 2.

(6) J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966); **16**, 969 (1963).

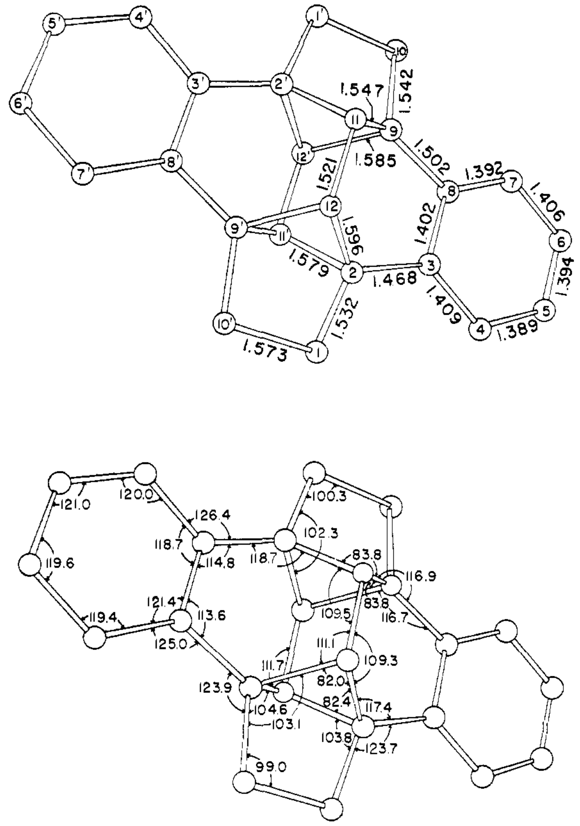

Figure 9. Bond distances and angles for dibenzoequinene.

The coordinates were subjected to a least-squares refinement in which the function $\Sigma w(F_o - F_c)^2$ was minimized, where $w = 1$ for all observed reflections. The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography," 1962. Owing to the possibility of a peroxide bridge across one of the benzene rings, there was some uncertainty concerning the identification of the two oxygen atoms in II. Therefore, the initial isotropic refinement was performed assuming that all atoms were carbon atoms. Peaks labeled O(1) and O(2) in Figure 1 exhibited much smaller temperature factors compared with the other atoms and were assigned as the oxygens. The refinement of the coordinates of dibenzoequinene proceeded in a straightforward manner. Several cycles of isotropic and anisotropic refinement resulted in R factors of 11.7% (1967 observed reflections) and 13.1% (1196 observed reflections) for II and IV, respectively. Difference maps computed at this stage in the refinement are shown in Figures 3 and 4. All ten hydrogens in the asymmetric unit for IV, and 24 of 26 for II, were located. The two hydrogens not found are bonded to C(24) in Figure 1. Table II lists the approximate hydrogen atom positions. The hydrogen atoms were included as constant parameters into the final anisotropic refinement which lowered the respective R factors to 9.7 and 10.9%.[7] The final coordinates and thermal parameters are tabulated in Tables III and IV.

Table IV. Fractional Coordinates and Anisotropic Thermal Parameters ($\beta_{ij} \times 10^4$) for Dibenzoequinene[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.2360	1.1533	0.4013	33	15	86	2	1	4
C(2)	0.3318	1.0140	0.4638	11	59	41	2	−4	−1
C(3)	0.2869	0.8586	0.5258	32	10	47	−5	9	−13
C(4)	0.1528	0.8121	0.5261	37	68	74	−19	20	−18
C(5)	0.1258	0.6616	0.5869	62	87	91	−35	33	−2
C(6)	0.2297	0.5554	0.6492	78	82	83	−39	38	−12
C(7)	0.3639	0.6005	0.6498	65	41	63	−14	16	−3
C(8)	0.3909	0.7508	0.5881	40	−7	51	−10	16	1
C(9)	0.5289	0.8149	0.5817	36	3	41	7	5	12
C(10)	0.6600	0.7174	0.6376	36	2	74	3	0	28
C(11)	0.5612	1.0005	0.6256	23	0	32	−3	2	−1
C(12)	0.4490	1.1201	0.5612	24	18	32	−7	0	−4
Standard error									
C	0.0004	0.0008	0.0004	4	16	5	6	3	6

[a] The thermal parameters are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Discussion

The ring systems, molecular configurations, and the orientations and relative magnitudes of the thermal ellipsoids are best seen by viewing the stereoscopic diagrams in Figures 5 and 6. In each product, the inner rings of the naphthalene system (I) have reacted forming two six-membered rings which have the boat conformation. The outer rings of the naphthalene system still retain their aromatic character.

The bond distances and angles for both molecules are displayed in Figures 7–9. The standard deviations based solely on the results of the least-squares refinement range from 0.008 to 0.013 Å for the bond distances in II, and from 0.006 to 0.009 Å for the bond distances in IV. The standard deviation of the angles is about 0.6° in each compound. Additional sources of error exist which are not accounted for in the least-squares refinement, so that the standard deviations are probably closer to twice the values quoted above. The larger deviations occur for the phenyl groups which have the larger thermal motion while the inner ring carbon atoms exhibit relatively isotropic motion. Fortunately, the parts of the molecules of greatest interest are the inner ring systems which have the least thermal motion, and are hence more accurately determined. The drawing in Figure 7 is not intended to portray the actual three-dimensional geometry, but serves to illustrate the fact that if one excludes the carbon atoms of the methoxy groups the molecule possesses an approximate mirror plane which passes vertically through the molecule and is perpendicular to the plane of the drawing. Three mutually perpendicular mirror planes are present in dibenzoequinene if the experimental uncertainty of the bond distances and angles is taken into account.

The mean C—C distance of the benzene rings in II is 1.391 Å, and 1.535 Å for the tetrahedrally bonded carbons. The analogous values in IV are 1.398 and 1.559 Å. The C=C bond in II is in the form of an ethylene bridge across one of the six-membered rings and has a length of 1.329 Å. The average C—C distance in cyclobutane in IV is 1.576 Å which is in agreement with previously reported values.[8]

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[7] Observed and calculated structure factors have been deposited as Document No. 9762 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[8] T. N. Margulis, *Acta Cryst.*, **19**, 857 (1965); I. L. Karle and J. Karle, *ibid.*, **20**, 555 (1966); T. B. Owen and J. L. Hoard, *ibid.*, **4**, 172 (1951); I. L. Karle, J. Karle, and K. Britts, *J. Am. Chem. Soc.*, **88**, 2918 (1966).

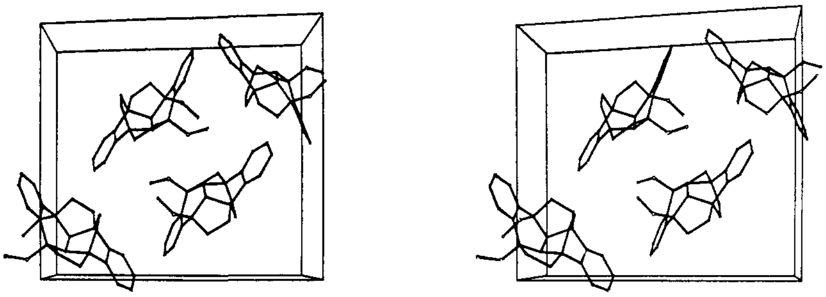


Figure 10. Stereoscopic diagram for the packing of the molecules in the unit cell for the dibenzodimethoxy compound. The horizontal axis is *b*, the vertical axis is *c*, and the axis approximately perpendicular to the paper is *a*.

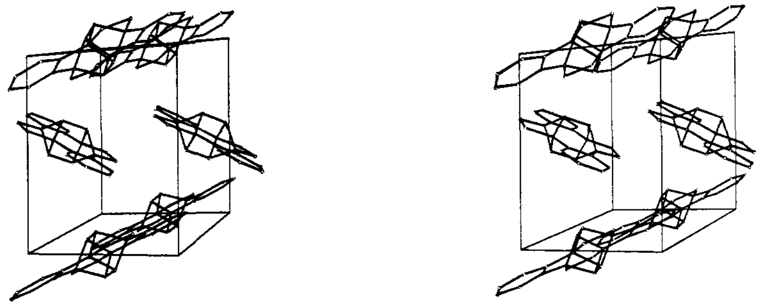


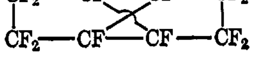
Figure 11. Stereoscopic diagram for the packing of molecules in the unit cell for dibenzoequinene. The horizontal axis is *b*, the vertical axis is *c*, and the axis approximately perpendicular to the paper is *a*.

Table V. Equations of the Least-Squares Planes and Angles between Them[a]

	Dibenzomethoxy Compound	
A	$1.7663x + 14.611y + 5.3290z = 3.6177$	C(1), C(2), C(3), C(4), C(5), C(6)
B	$3.1291x + 12.892y + 6.5751z = 6.7261$	C(17), C(18), C(19), C(20), C(21), C(22)
C	$1.9891x + 14.963y + 4.0891z = 3.5525$	C(10), C(5), C(6), C(7)
D	$3.3759x + 11.682y + 7.8735z = 5.6168$	C(7), C(8), C(9), C(10)
E	$4.2988x - 3.5762y + 11.776z = 5.5554$	C(13), C(9), C(8), C(16)
F	$3.2186x + 12.472y + 7.0691z = 6.7545$	C(16), C(17), C(18), C(13)
G	$-1.0424x + 15.298y - 4.3419z = 1.1521$	C(13), C(14), C(15), C(16)
Angle between planes		
C–D 158.5°	*D–E* 120.8°	*F–G* 122.1°
E–F 116.5°	*E–G* 121.4°	
	Dibenzoequinene	
M	$-1.3228x + 3.8253y + 8.7992z = 7.5316$	C(3), C(4), C(5), C(6), C(7), C(8)
N	$-1.1346x + 3.5648y + 8.9612z = 7.4365$	C(1), C(2), C(9′), C(10′)
P	$-6.6876x + 5.9319y + 1.6669z = 4.5768$	C(2), C(12), C(9′)
Q	$5.4617x - 2.5145y + 6.6166z = 2.3605$	C(2), C(11′), C(9′)
R	$-1.3671x + 3.7240y + 8.8711z = 7.4742$	C(2), C(3), C(8), C(9)
S	$-6.1875x - 1.0216y + 8.9379z = 1.0952$	C(2), C(12), C(11), C(9)
T	$4.2557x + 6.2052y + 3.6460z = 9.4199$	C(2), C(11′), C(12′), C(9)
Angle between planes		
P–Q 124.5°	*R–T* 135.2°	
R–S 134.6°	*S–T* 90.0°	

[a] The equations are referred to the monoclinic axes and the value on the right-hand side is the origin-to-plane distance in Å. V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, **12**, 600 (1959). The coordinates in Tables III and IV may be substituted directly into these equations.

The constraints imposed by the inner ring system cause large deviations from the tetrahedral value for the bond angles. This is most evident in dibenzoequinene where the largest deviations occur in the cyclobutane ring, the average CCC angle being 83.0°. A highly puckered cyclobutane ring has also been found in C_8F_{12}[9]



where the average CCC angle is 81.5°. C_8F_{12} consists of a puckered four-membered ring in the middle which is fused to five-membered rings on either side and has a configuration similar in many respects to the inner ring system of dibenzoequinene. Other molecules containing four-membered rings distorted from the ideal square configuration whose structures have been reported have CCC angles of the order of 87°.[8,10] Thus dibenzoequinene and C_8F_{12} appear to be unique in possessing so highly distorted cyclobutane rings. Large deviations from the tetrahedral value also occur in the cyclo-

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(9) I L. Karle, J. Karle, T. B. Owen, and J. L. Hoard, *Acta Cryst.*, 18, 345 (1965).

(10) Y. Okaya and A. Bednowitz, *ibid.*, 22, 111 (1967).

pentane rings. The values of the angles in dibenzoequinene are in agreement with those reported for C_8F_{12}.

The equations of the important least-squares planes and the angles between them are given in Table V. In dibenzoequinene, the dihedral angle between planes which contain atoms C(2), C(12), C(9′) and C(2), C(11′), C(9′) is 124.5°. This compares with the angle of 120° which was obtained in C_8F_{12}. The equivalent angle in other compounds which contain cyclobutane rings ranges from 150 to 162°. The largest deviation of an atom from the plane through atoms C(1), C(2), C(9′), C(10′) in IV is 0.003 Å, with atoms C(12) and C(11′) located approximately 1.0 Å above and below this plane, respectively. Atoms C(7), C(24), C(23), C(16) and C(10), C(11), C(12), C(13) in II are not coplanar, 0.2 Å being the largest deviation of an atom from the least-squares planes. The phenyl rings are essentially planar, 0.02 Å being the largest deviation in II, and 0.003 Å the largest deviation in IV.

Figures 10 and 11 illustrate the packing in the unit cells. Excluding hydrogens, there are no intermolecular contacts smaller than 3.75 Å in II and none less than 3.66 Å in IV. Such relatively large intermolecular separations suggest that the major distortions of the molecules from the mirror planes are probably the result of intramolecular effects or random errors, even though intermolecular effects may still be important at these separations.

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Solvent Effects in Electroneutral Reactions. I. Combination and Disproportionation of Ethyl Radicals in Solution

Andrew P. Stefani

Contribution from the Department of Chemistry, The University of Mississippi, University, Mississippi 38677. *Received August 7, 1967*

Abstract: The rate ratio k_d/k_c of the disproportionation–combination reaction couple of ethyl radicals was measured at 65° in ten different solvents. The logarithms of these ratios are linear functions of the square root of the cohesive energy density of the solvents. The reaction couple was investigated in the gas phase from −65 to +80° in vessels of variable volume, and it was found that a considerable extent of the reaction proceeds by a heterogeneous mechanism. On the basis of these observations the temperature dependence of k_d/k_c in liquid and in solid reaction media is interpreted to be a consequence of a secondary thermal effect whose origin is the internal volume change of the medium. The rates of certain other polar reactions are discussed in terms of internal volume considerations.

The influence of solvents upon reaction rates and equilibria has been discussed extensively in the literature in the past few decades and, although the distinction between ionic, polar, and nonpolar mechanisms had been recognized at a rather early stage in the development of reaction rate theories, nearly all the emphasis in this connection has been placed upon ionic and highly polar reactions. Although the necessary groundwork has been laid for the quantitative treatment of the influence of solvents upon the rates of electroneutral[1] reactions and of certain other reactions which manifest similar kinetic behavior, relatively few examples of such systems have been studied in a wide range of solvents to permit meaningful generalizations.

In the discussion of solvent effects upon reaction rates, regardless of which model of a liquid one employs, at least two general factors are always necessary in the theoretical development, namely the factor giving rise to the internal volume effects and the factor giving rise to the solvation effects.[2-5] Of these two factors the first accounts for the restrictions imposed upon the spatial requirements of the reacting species by the self-cohesion of the solvent, and also for the restrictions imposed upon the external degrees of freedom of these species by the solvent due to crowding. The second factor contains all other effects, most of which, in the absence of certain specific interactions, are consequences of the dielectric properties of the solvent. However, since the multitude of molecular interaction mechanisms which are responsible for the cohesive forces in the liquid state are fundamentally electrostatic in nature and inasmuch as polarity and polarization phenomena pervade all molecular interactions, no line of demarcation separating electroneutral from polar changes can be defined in an unambiguous manner. Obviously these two factors are not mutually exclusive, but they may be treated as limiting cases of the general relations pertaining to

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(1) An electroneutral reaction is one in which all of the participating species are neither ionic nor highly polar; when studied in solution, the reacting system conforms to the principles that characterize regular solution; *cf.* J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

(2) S. Glasstone, K. J. Laider, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(3) R. A. Ogg, Jr., and O. K. Rice, *J. Chem. Phys.*, 5, 140 (1937).

(4) (a) W. F. K. Wynne-Jones and H. Eyring, *ibid.*, 3, 492 (1935); (b) C. E. Waring and P. Becher, *ibid.*, 15, 488 (1947).

(5) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 32, 1333 (1936).