What role do electrostatic interactions have in determining changes in the infrared spectrum of donor–acceptor complexes? (2) Are electrostatic interactions as important in π–π-type complexes as they are in the benzene–halogen complexes? (3) Are electrostatic interactions important in determining the relative stability of a series of complexes using the same acceptor and different donors? (4) Are the logical consequences of the inclusion of electrostatic interactions borne out by experiment? For example, on the basis of electrostatic considerations, one predicts that a benzene–krypton complex should have about half the stability of the benzene–chlorine complex. (5) Can the repulsion contribution to the energy be reliably estimated? These questions will be discussed in forthcoming papers of this series.
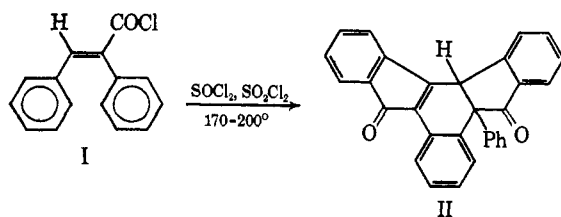
The Crystal and Molecular Structure of 14c-Hydro-5a-phenylbenz[a]indeno[2,1-c]fluorene-5,10-dione (C₃₀H₁₈O₂)[1]

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Abstract: α-Phenylcinnamoyl chloride (I) upon pyrolysis with thionyl chloride forms 14c-hydro-5a-phenylbenz-[a]indeno[2,1-c]fluorene-5,10-dione ($C_{30}H_{18}O_2$) (II). The chemical properties and ultraviolet and infrared spectra of II closely approximate those of indones. An X-ray structure analysis was performed in order to unequivocally establish the molecular structure. Data from a single crystal ($P2_1/a$, $a = 19.65 \pm 0.01$ A, $b = 10.55 \pm 0.01$ A, $c = 10.86 \pm 0.01$ A, $\beta = 111° 20' \pm 5'$, $Z = 4$) were collected using a four-circle diffractometer operating under control of a time-shared SDS 920 computer (Brookhaven Multiple Spectrometer Control System, MSCS). The structure was directly determined from the diffraction data using the symbolic addition method of phase determination. The complete molecule (II) was found from the E map based on the unique set of phases obtained. Least-squares and Fourier methods were used for refinement and hydrogen atom location. The molecule is acentric, with the racemic stereoisomers crystallizing in an ordered arrangement. The molecule consists of two planes intersecting along the Ph–C–CH bond.

New procedures for the formation of carbon-to-carbon bonds are of great interest and importance in organic chemistry. The present investigation is concerned with a novel one-step procedure which has been shown to result in the creation of four such bonds between two molecules of α-phenylcinnamic acid in such a way as to produce a system of six fused carbocyclic rings. The unusual chemistry of compounds contain-

ing this system and related systems will be the subject of subsequent reports. The present paper deals with the preparative procedure, with the chemical and spectro-

scopic evidence which permitted postulation of a preliminary structure for the first product of this type to be obtained, and particularly with the methods of X-ray crystallographic analysis which independently and finally provided a complete elucidation of the structure of the pentacyclic product.

The product in question is formed under relatively mild conditions, and we first encountered it inadvertently. During an attempt to prepare pure α-phenylcinnamoyl chloride (I) by reaction, over a steam bath, of the corresponding carboxylic acid with thionyl chloride in the presence of small amounts of sulfuryl chloride, the steam services to the laboratory were shut down. Since the reaction was already in progress, it was completed employing a Bunsen burner. After refluxing for 30 min in the presence of excess chlorinating reagent, the excess was removed by distillation. Toward the end of the distillation, the pot temperature rose to 160°, and a vigorous reaction ensued. Hydrogen chloride was evolved in large quantities, and the contents of the flask turned red and, upon cooling, formed a red glass. After two recrystallizations from glacial acetic acid, red-orange prismatic crystals melting at 253–255° were obtained. This phenomenon had never been encountered in our previous preparations of α-phenylcinnamoyl chloride using the same method
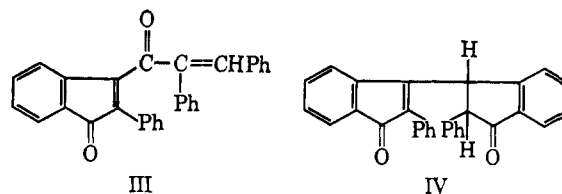
at steam-bath temperatures. A search of the literature revealed that Blum-Bergmann[3] had observed the same reaction. She found that the compound had the composition $C_{15}H_{10}O$ and that the molecular weight corresponded to the formula $C_{30}H_{20}O_2$. Tentatively she suggested that the structure might be that of 2-phenyl-3-(α-phenylcinnamoyl)indone (III). For ease in communication, we called the red compound "phenylcinnamalone." Our analysis gave the empirical formula as $C_{15}H_{9-10}O$, and Rast molecular weight determinations were in agreement with the molecular formula $C_{30}H_{18-20}$-O_2, thus confirming Blum-Bergmann's data. However, phenylcinnamalone showed no addition reactions which might be considered typical of the α-phenylcinnamoyl group, and its infrared spectrum showed only a single carbonyl band at 1710 cm^{-1}.

Phenylcinnamalone formed a monophenylhydrazone. The infrared spectrum of the monophenylhydrazone retained a single carbonyl band at 1710 cm^{-1}. Reduction of phenylcinnamalone by the Wolff–Kishner method yielded a hydrocarbon having the molecular formula $C_{30}H_{22}$. It was thus indicated that both oxygens were carbonyl functions.

Oxidation of phenylcinnamalone with nitric acid yielded o-phthalic acid.[4] This supplied evidence that perhaps the molecule contained benzene nuclei fused to other cyclic moieties *via* an o-carbonyl group. Assuming this conclusion to be valid, we decided to compare the infrared spectra of various substituted benzene ketonic derivatives with that of phenylcinnamalone.

Acetophenone and other analogous open-chain ketones show carbonyl absorption at 1680–1700 cm^{-1}.[5] α-Tetralones have carbonyl absorption at about 1680–1695 cm^{-1},[6,7] and benzsuberones show carbonyl absorption at about 1675 cm^{-1}.[7] Indones and indanones have carbonyl absorption at 1710–1725 cm^{-1}.[6] Indones show a carbonyl band at 1710 cm^{-1},[8–10] and the position of this band is particularly specific among 2-phenyl-3-substituted indones.[8–10] In addition, several indones were prepared[11,12] and their infrared spectra taken; 2,3-diphenylindone, 2-phenyl-3-benzylindone, and 2-phenyl-3-carbamoylindone all showed ketone carbonyl absorption at 1710 cm^{-1}. On this basis, a carbonyl group was ascribed to be present in an indone system. Using these data, a guess (IV) concerning the structure of phenylcinnamalone was made.

Structure IV fits the observed molecular formula and the requirement that an indone nucleus be present. Further, the nature of structure IV is such that it might be expected that the infrared carbonyl absorptions might overlap. However, from the proton magnetic resonance (pmr) spectrum it appeared that IV was not

(3) O. Blum-Bergmann, *Ber.*, **65**, 109 (1932).
(4) R. A. Kropf, Doctoral Dissertation, Carnegie Institute of Technology, Pittsburgh, Pa., 1957, p 77.
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(6) D. Cook, *Can. J. Chem.*, **39**, 31 (1961).
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(9) M. Jasein and N. Fuson, *Bull. Soc. Chim. France*, [5] **19**, 389 (1952).
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(11) D. Coe, M. Gale, R. Linstead, and C. Timmons, *J. Chem. Soc.*, 123 (1957).
(12) C. F. H. Allen, J. W. Gates, Jr., and J. A. Van Allan, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 353.

III   IV

the correct structure because the only nonaromatic peak, at τ 5.36, appears as a singlet. An intense complex multiplet was centered at about τ 2.78. Integration showed a ratio of 18:1 for aromatic to nonaromatic protons. In the light of the pmr evidence, structure IV did not appear to be quite correct, and it was decided to attempt the structure determination by X-ray crystallographic methods, and, as is subsequently shown, phenylcinnamalone has the structure II.

This simple preparation of such a complicated novel ring system is intriguing, and we have started to prove its generality by the synthesis of analogs.

Experimental Section

Preparation of Phenylcinnamalone (II). Five grams (0.0223 mole) of α-phenylcinnamic acid was dissolved in a mixture containing 48.0 ml of thionyl chloride and 2.0 ml of sulfuryl chloride. The resulting mixture was refluxed for 30 min, after which time the excess thionyl chloride was removed by distillation. The flask was then heated slowly to 195°. At 165° there was a vigorous reaction, and the temperature rose quickly to 190–195°. Heating for an additional 3–4 min resulted in a dark red oil, which solidified on cooling. The solid was crystallized from 50 ml of acetic acid. Bright orange crystals, melting at 253–254°, resulted. The average yield was 2.0 g (43.7%).

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.20; H, 4.69. Found: C, 87.11; H, 4.50. Infrared data (cm^{-1}): 3012 w, 1938 s, 1710 s, 1602 s, 1488 w, 1462 m, 1453 w, 1388 w, 1366 w, 1309 w, 1282 m, 1253 w, 1174 w, 1163 w, 1149 w, 1131 w, 1106 w, 1087 w, 1050 w, 1042 w, 1029 w, 1020 w, 1004 w, 958 w, 936 w, 912 w, 890 m, 877 w, 853 w, 828 w.

Wolff–Kishner Reduction of Phenylcinnamalone (II) to 14c-Hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene ($C_{30}H_{22}$). The reduction was a modification of the Huang–Minlon procedure. One gram (0.0024 mole) of phenylcinnamalone was dissolved, as completely as possible, in 20 ml of diethylene glycol. To this suspension was added 18 ml of hydrazine hydrate (85%). The mixture was then refluxed for 3.5 hr. At the end of this time 4.0 g of solid potassium hydroxide was cautiously added to the hot solution, and refluxing was continued for another 30 min. The reflux condenser was then removed and the temperature permitted to rise to 190–200°, where refluxing was continued for 1 hr. The solution was cooled and poured into 200 ml of water. Three extractions with 30-ml portions of ether gave a yellow solution which was washed with water and dried (CaSO$_4$). Evaporation of the ether left an oil which solidified on trituration with 95% ethanol. Crystallization of the solid from benzene–95% ethanol or acetic acid gave pale yellow crystals melting at 236–237°. The yield was 61 mg (6.6%).

Anal. Calcd for $C_{30}H_{22}$: C, 94.22; H, 5.80. Found: C, 94.00; H, 5.66.

Phenylcinnamalone Phenylhydrazone. To 2.0 g (0.00488 mole) of phenylcinnamalone was added 20 ml of phenylhydrazine and 10 drops of glacial acetic acid. The mixture was heated for 30 min on a steam bath. After the heating period, 50 ml of 95% ethanol was added, and a homogeneous solution resulted. After cooling for 4 hr at 20°, 2.1 g (84.3%) of phenylcinnamalone phenylhydrazone crystallized. Three recrystallizations from 20% dioxane–80% ethanol gave the compound as the hemihydrate melting at 270–271°.

Anal. Calcd for $C_{36}H_{25}ON_2 \cdot 0.5H_2O$: C, 84.61; H, 5.10; N, 5.49. Found: C, 84.64; H, 5.17; N, 5.46.

Crystallography. A primsatic, monoclinic, red-orange crystal of phenylcinnamalone was mounted with the *b* axis parallel to the axis of a standard goniometer head. The space group is P2$_1$/c with four molecules per unit cell. The cell parameters were found to be a = 19.65 ± 0.01 A, b = 10.55 ± 0.01 A, c = 10.86 ± 0.01 A, β = 111° 20′ ± 5′, V = 2097 ± 6 A^3. The X-ray density is 1.30 g/cm^3. The cell parameters were determined and intensity measure-

ments were made with Ni-filtered Cu Kα radiation (λ 1.5418 Å).

Intensity data were obtained on a four-circle diffractometer under computer control of the Brookhaven Multiple Spectrometer Control System.[13] A user program for Automatic X-ray Data Aquisition (AXDA) was written to operate under this system and to time share an SDS 920 computer with eight neutron diffraction experiments.[14] About 4600 Bragg peaks including equivalent and repeat measurements were step scanned to obtain the integrated intensities. These were reduced off-line to 2162 independent integrated intensities. About 1740 reflections were above the minimum observable. All off-line data processing and computation on the automatically obtained data were carried out with the aid of the CDC 6600 computer at the Brookhaven National Laboratory. No absorption correction was applied. An estimated absolute scale factor and mean isotropic temperature factor were obtained by Wilson's method.[15] The normalized structure factor magnitude $|E_H|$ were computed using the relation

$$E_H{}^2 = F_H{}^2/\epsilon\sum_j f_j{}^2 \qquad (1)$$

where ϵ is unity for all reflections other than $h0l$ and $0k0$, for which $\epsilon = 2.0$. The summation of the squared atomic scattering factors $f_j{}^2$ is over all atoms in the unit cell. The F's are on an absolute scale and corrected for thermal motion. Only 665 normalized structure factors had magnitudes greater than 1.0 and were used in the phase determination.

Structural Analysis

Phase Determination. As the crystal was centrosymmetric the most straightforward method of structure analysis was to utilize the symbolic addition method[16,17] to determine the phase directly from the normalized structure factor magnitudes.

A computer program SORTE, written in FORTRAN IV, was used to aid the implementation of the symbolic addition procedure.[18,19] The basic phase relation used by this procedure is the Σ_2 formula[20]

$$sE_H \sim s\sum_K E_K E_{H-K} \qquad (2)$$

where "s" means "sign of." This formula describes the phase interaction between the primary reflections H and all other interacting pairs K, H–K. The symbolic addition procedure requires only a few initial signs in order to determine enough additional signs by relation 2 so that the main features of the structure can be obtained by Fourier analysis.

The starting set of symbols used in the present study, including three reflections chosen with arbitrary (+) sign to fix the origin, is listed in Table I. The first

Table I. Starting Set of Assigned Signs and Symbols

Phases	hkl	E
+	32$\bar{1}$	4.36
+	83$\bar{1}$	3.90
+	44$\bar{1}$	2.89
a	42$\bar{1}$	3.51
b	10 4 $\bar{2}$	2.92
c	82$\bar{9}$	3.41
d	47$\bar{6}$	2.82

symbols assigned after the origin fixing signs were a and b. The phase-determining procedure did not progress far before it was necessary to introduce additional symbols. After assigning c and subsequently d, the process ran smoothly. Early indications that b was equivalent to (−) allowed the number of working symbols to be reduced to three. Near the end of the phase-determining process, there were many relations evident among the symbols, suggesting the sign values a = +, c = +, and d = −.

With these values inserted for the symbols, 600 phases were determined for $|E|$ greater than 1.0 (65 were indeterminate). Using these phases an E map was computed, and an automatic peak search listed the maxima of the map in decreasing magnitude. The 32 largest peaks directly gave the positions in the unit cell of the 32 heaviest atoms (carbon and oxygen).

Refinement. Starting with the coordinates of the carbon and oxygen atoms found from the E map, a full-matrix least-squares refinement using isotropic temperature factors resulted in an R factor of 0.14 after three cycles. A difference electron density synthesis resulted in the location of 18 hydrogen atoms.

With the hydrogen coordinates fixed, the heavier atoms were subjected to least-squares refinement of the positional parameters and anisotropic temperature factors. Finally the hydrogen atoms with isotropic temperature factors were introduced, and the refinement was allowed to proceed until the variation of hydrogen parameters from cycle to cycle was less than half their estimated standard deviation. The final shifts in the heavier atom positions were less than one-tenth of their respective standard deviations. At the termination of refinement the error index

$$R = \sum||F_o| - |F_c||/\sum|F_o|$$

was 0.074.[21]

The atomic scattering factors used in the structure factor calculations were obtained from the "International Tables for X-ray Crystallography."[22] The weights used in the least-squares refinement were inversely proportional to standard deviations estimated from the counting statistics plus a factor proportional to the intensity.

$$\sigma^2(I - B) = I + B + [0.03(I - B)]^2 \qquad (3)$$

Unobserved reflections were given zero weight.

The final atomic coordinates, their standard deviations, and thermal parameters are shown in Table II. After checking the phases in the final structure factor calculation, it was found that 18 of the 600 reflections whose signs were directly determined had originally been assigned an incorrect phase. Most of the incorrect phases were associated with small $|E|$ (less than 1.5).

(13) D. R. Beaucage, M. A. Kelly, D. Ophir, S. Rankowitz, R. J. Spinrad, and R. Van Norton, *Nucl. Instr. Methods*, **40**, 26 (1966).

(14) A. L. Bednowitz, P. Coppens, and W. C. Hamilton, Abstracts of the Pittsburgh Diffraction Conference, Nov 1966.

(15) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

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(17) J. Karle and I. L. Karle, *ibid.*, **21**, 849 (1966).

(18) A. L. Bednowitz and B. Post, *ibid.*, **21**, 566 (1966).

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

(20) J. Karle and H. Hauptman, *ibid.*, **3**, 181 (1950).

(21) The table of observed and calculated structure factors was submitted with the manuscript and has been deposited with the U. S. Library of Congress as Document No. 9667. Requests for copies should be addressed to: Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for microfilm or $1.25 for electrostatic positive prints. Advance payment is required. Make checks or money orders payable to: Photoduplication Service, Library of Congress.

(22) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

Discussion

The direct determination of this crystal structure led to the unambiguous solution of the molecular structure of $C_{30}H_{18}O_2$. It is composed of three planes intersecting at the tetrahedral carbon atom (5a). (The atom numbering sequence is given in Figure 1). Figure 2 is a stereo-pair drawing prepared with the aid of a computer.[23]
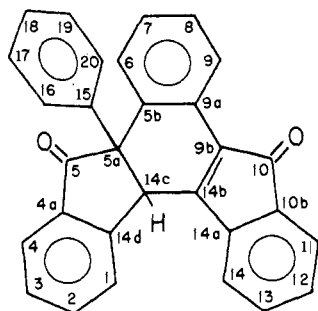

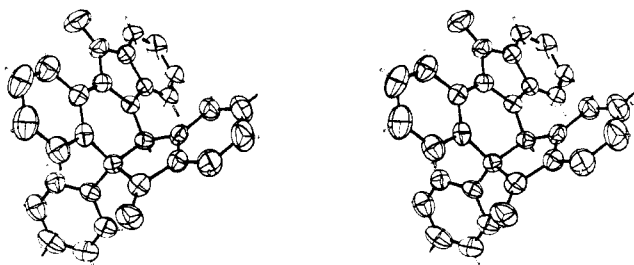Figure 1. Schematic diagram of the molecule showing the numbering system.

Figure 2. Stereo-pair drawing of the molecule showing the orientation and relative magnitude of the vibrational ellipsoids. The location of the hydrogen atoms is suggested by short stick bonds.

It shows the molecular configuration, the three intersecting planes, and the orientation and relative magnitude of the thermal ellipsoids.

The fluorene and the indeno group intersect with a dihedral angle of about 117°. The plane of the phenyl group is nearly at right angles to the other two groups. The structure of the molecule is in agreement with indirect deductions based on various physicochemical methods discussed above.

Consider the two carbon atoms 5a and 14c. There are four distinguishable permutations of the six ligands about this bonded pair. Because of the formation of near-planar rings, only two isomers are sterically possible. Both isomers, related by the center of symmetry, appear in this racemic crystal. The isomeric molecules crystallize in layers of alternate handedness. This can be seen in the stereo-pair drawing of the crystal packing (Figure 3).

The region around the pair of carbon atoms 5a–14c is severely strained. This is attested to by the abnormally long single bond of 1.583 A. (Figure 4 shows the bond lengths and angles in this region.) The bond from the tetrahedral carbon atom 5a to carbon atom 5 of the carbonyl group (1.556 A) is also longer than normal for a single bond. In Figure 5 the bond lengths and angles for the indeno group are shown. In this group the five-

(23) C. K. Johnson, Oak Ridge National Laboratory Report ORNL-3794, 1965.

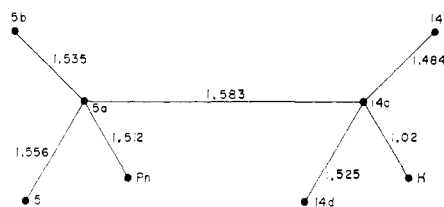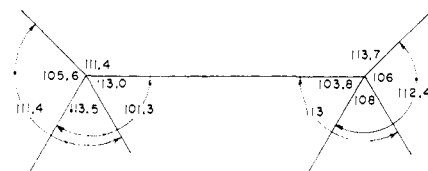Figure 3. Stereo-pair drawing of the crystal packing with one unit cell superimposed.

Figure 4. Bond distances and angles around the tetrahedral carbon atoms.
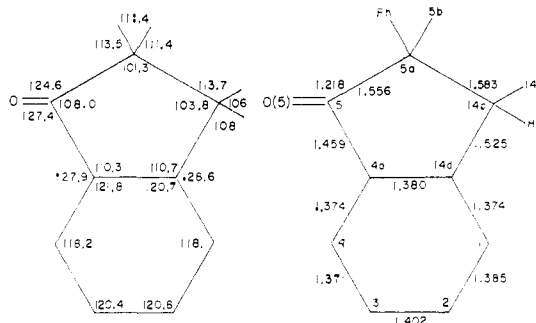

Figure 5. Bond distances and angles in the indeno group containing the puckered five-membered ring.

membered ring is puckered with the apex carbon (5a) about 0.5 A out of the plane. The apex angle is narrower (101.3°) than the apex angle in the unsaturated five-membered ring (107.9°) (Figure 6). The benz group in Figure 5 is planar as expected with deviations from the plane of eq 4 being less than 0.005 A. The devia-

$$7.94x - 9.61y - 0.781z = 0.843 \qquad (4)$$

tions of atoms 5 and 14c are about −0.07 and +0.02, respectively, with the oxygen out of the plane by about 0.1 A.

The entire indeno group in Figure 6 is planar (eq 5) with the largest deviation about −0.03 for the apex atom 9b.

$$15.6x + 6.39y - 3.04z = 3.97 \qquad (5)$$

The benz group in Figure 7 is planar (eq 6) with deviations of less than 0.008 A. From the close agreement

$$16.1x + 5.89y - 1.99z = 3.85 \qquad (6)$$

between the coefficients in eq 5 and 6, it can be seen that the benz group and the second indeno group

Table II. Atomic Coordinates and Anisotropic Temperature Factors

(a) Atomic coordinates and estimated standard deviations[a]

Atom	x	y	z	Atom	x	y	z
—Benzindenofluorenedione group—				—Hydrogen atoms—			
C(1)	3479 (2)	1973 (4)	0312 (4)	H(1)	3277 (20)	1789 (35)	−0723 (39)
C(2)	4168 (3)	2496 (6)	0907 (5)	H(2)	4424 (20)	2870 (36)	0339 (36)
C(3)	4480 (3)	2635 (6)	2283 (5)	H(3)	4957 (23)	2973 (38)	2669 (40)
C(4)	4104 (2)	2264 (5)	3065 (5)	H(4)	4316 (20)	2399 (35)	4054 (39)
C(4a)	3419 (2)	1752 (4)	2462 (4)				
C(5)	2912 (2)	1333 (4)	3080 (4)				
C(5a)	2147 (2)	1157 (3)	1973 (3)				
C(5b)	1742 (2)	2414 (4)	1913 (4)				
C(6)	1700 (2)	2922 (4)	3076 (4)	H(6)	1941 (21)	2485 (36)	3855 (39)
C(7)	1310 (3)	4004 (5)	3067 (6)	H(7)	1270 (20)	4320 (36)	3933 (38)
C(8)	0939 (3)	4597 (5)	1895 (6)	H(8)	0686 (21)	5326 (38)	1894 (37)
C(9)	0969 (3)	4136 (4)	0735 (5)	H(9)	0729 (21)	4559 (37)	−0088 (39)
C(9a)	1371 (2)	3037 (4)	0722 (4)				
C(9b)	1397 (2)	2517 (4)	−0493 (4)				
C(10)	0983 (2)	2911 (4)	−1902 (4)				
C(10b)	1202 (2)	1992 (4)	−2724 (4)				
C(11)	0980 (3)	1884 (5)	−4072 (4)	H(11)	0647 (21)	2530 (35)	−4707 (38)
C(12)	1268 (3)	0910 (6)	−4572 (5)	H(12)	1136 (21)	0714 (38)	−5477 (13)
C(13)	1775 (3)	0082 (5)	−3764 (5)	H(13)	1960 (20)	−0622 (37)	−4093 (39)
C(14)	2004 (2)	0198 (4)	−2396 (4)	H(14)	2414 (20)	−0410 (37)	−1670 (38)
C(14a)	1715 (2)	1149 (4)	−1886 (4)				
C(14b)	1823 (2)	1524 (3)	−0511 (4)				
C(14c)	2361 (2)	0973 (4)	0715 (3)	H(14c)	2410 (21)	0043 (37)	0506 (38)
C(14d)	3111 (2)	1597 (4)	1109 (4)				
O(I)	3043 (2)	1162 (3)	4253 (3)				
O(II)	0561 (2)	3780 (3)	−2287 (3)				
—Phenyl group—							
C(15)	1722 (2)	0050 (4)	2211 (4)				
C(16)	2079 (3)	−1043 (4)	2848 (4)	H(16)	2593 (22)	−0957 (36)	3062 (37)
C(17)	1696 (3)	−2032 (5)	3107 (4)	H(17)	1979 (21)	−2776 (38)	3596 (38)
C(18)	0955 (3)	−1950 (5)	2756 (5)	H(18)	0737 (20)	−2618 (35)	3136 (37)
C(19)	0591 (3)	−0897 (5)	2086 (5)	H(19)	0171 (21)	−0870 (36)	1931 (38)
C(20)	0967 (2)	0089 (4)	1812 (4)	H(20)	0689 (20)	0816 (37)	1334 (38)

(b) Anisotropic and isotropic temperature factors[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Hydrogen	B, A
C(1)	33 (2)	140 (6)	98 (5)	0 (3)	28 (2)	16 (4)	H(1)	3.2 (0.9)
C(2)	35 (2)	206 (8)	152 (7)	−13 (3)	35 (3)	37 (6)	H(2)	3.6 (0.9)
C(3)	30 (2)	235 (9)	139 (7)	−21 (3)	17 (3)	8 (6)	H(3)	5.1 (0.9)
C(4)	33 (2)	177 (7)	100 (6)	−6 (3)	12 (3)	1 (5)	H(4)	2.6 (0.9)
C(4a)	25 (1)	106 (5)	95 (5)	1 (2)	16 (2)	6 (4)		
C(5)	32 (1)	92 (5)	81 (5)	−1 (2)	17 (2)	−18 (4)		
C(5a)	24 (1)	79 (4)	68 (4)	−2 (2)	13 (2)	−4 (3)		
C(5b)	24 (1)	86 (5)	107 (5)	−3 (2)	24 (2)	−12 (4)		
C(6)	40 (2)	104 (5)	105 (6)	−6 (3)	32 (3)	−22 (5)	H(6)	1.2 (1.0)
C(7)	43 (2)	123 (7)	171 (7)	0 (3)	39 (3)	−55 (6)	H(7)	4.0 (0.9)
C(8)	37 (2)	106 (6)	196 (9)	11 (3)	28 (3)	−46 (6)	H(8)	3.3 (1.0)
C(9)	35 (2)	91 (5)	151 (7)	2 (3)	24 (3)	−20 (5)	H(9)	3.6 (1.0)
C(9a)	24 (1)	72 (5)	103 (5)	−3 (2)	15 (2)	−9 (4)		
C(9b)	26 (1)	77 (5)	86 (5)	−1 (2)	15 (2)	5 (4)		
C(10)	24 (1)	100 (5)	119 (6)	3 (2)	11 (2)	18 (4)		
C(10b)	25 (1)	114 (5)	78 (5)	−2 (2)	9 (2)	34 (4)		
C(11)	35 (2)	184 (7)	86 (6)	5 (3)	9 (3)	34 (5)	H(11)	3.2 (0.9)
C(12)	42 (2)	237 (9)	72 (6)	−9 (4)	14 (3)	−18 (6)	H(12)	4.1 (1.0)
C(13)	41 (2)	179 (7)	91 (6)	12 (3)	21 (3)	−14 (5)	H(13)	4.7 (1.0)
C(14)	36 (2)	130 (6)	79 (5)	−8 (3)	18 (2)	−9 (4)	H(14)	1.1 (0.9)
C(14a)	24 (1)	97 (5)	77 (5)	−4 (2)	15 (2)	2 (4)		
C(14b)	29 (1)	81 (5)	79 (5)	−2 (2)	19 (2)	4 (4)		
C(14c)	30 (1)	78 (5)	63 (4)	1 (2)	15 (2)	1 (4)	H(14c)	1.0 (1.0)
C(14d)	22 (1)	104 (5)	76 (5)	9 (2)	10 (2)	2 (4)		
O(I)	42 (1)	170 (4)	65 (3)	−10 (2)	15 (2)	−5 (3)		
O(II)	49 (1)	144 (4)	147 (5)	33 (2)	15 (2)	39 (4)		
—Phenyl group—								
C(15)	35 (2)	93 (5)	60 (4)	−4 (2)	20 (2)	−3 (4)		
C(16)	42 (2)	97 (5)	100 (5)	−7 (3)	26 (3)	−6 (4)	H(16)	1.2 (1.0)
C(17)	55 (2)	105 (6)	114 (6)	−1 (3)	30 (3)	6 (5)	H(17)	2.3 (1.0)
C(18)	72 (3)	113 (6)	137 (7)	−30 (4)	55 (5)	−14 (5)	H(18)	4.8 (0.9)
C(19)	48 (2)	118 (7)	168 (8)	−20 (3)	50 (3)	−26 (5)	H(19)	4.6 (1.1)
C(20)	34 (2)	82 (5)	117 (6)	−4 (2)	30 (3)	−6 (4)	H(20)	2.6 (1.0)

[a] All times 10^4. [b] The β's are used in the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The anisotropic temperature factors have been multiplied by 10^4.
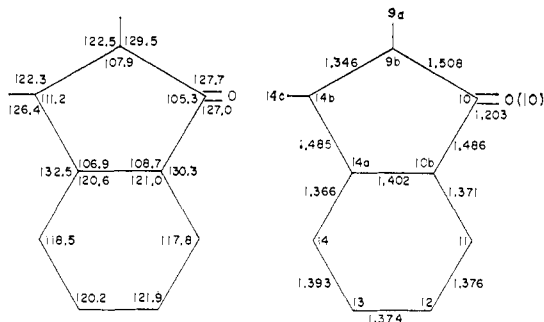
Figure 6. Bond distances and angles in the second indeno group with the planar five-membered ring.
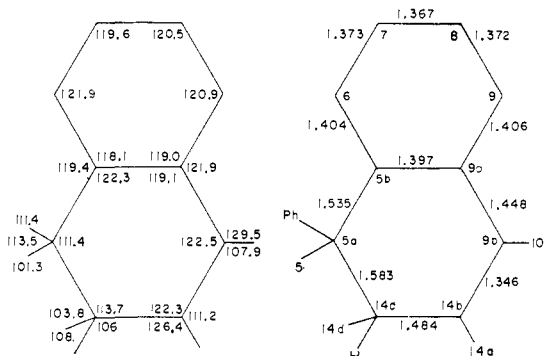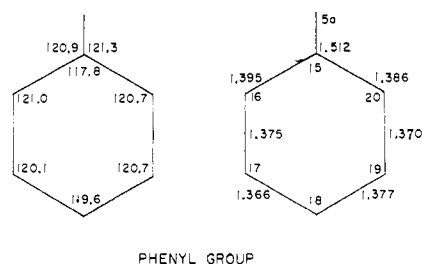

Figure 7. Bond distances and angles in the benz group and central six-membered ring.

are nearly coplanar. When a least-squares plane was computed including both groups (eq 7), the maximum deviation from planarity was 0.1 A. The central six-

$$15.9x + 6.17y - 2.52z = 3.83 \qquad (7)$$

membered ring is puckered with deviations from the plane of the benzfluorenone grouping amounting to −0.2 A for atom 5a and +0.3 A for atom 14c. The

PHENYL GROUP

Figure 8. Bond distances and angles in the phenyl group.

deviations from the plane (eq 8) of the phenyl group in Figure 8 are less than 0.02 A.

$$-4.58x + 4.42y + 9.80z = 1.38 \qquad (8)$$

The bond lengths in the six-membered central group shown in Figure 7 are interesting for the variation they exhibit. They vary from 1.346 A for the double bond 14b–9b to 1.583 for the long single bond 5a–14c. The magnitude of the estimated standard deviations for bond lengths was found to be of the order of ±0.005 A for bonds between the heavier atoms. The estimated deviations for bond angles involving only the carbon and oxygen atoms is of the order of ±0.4°.

The peripheral atoms exhibit anisotropic motion with amplitudes larger than those in the center of the molecule which in addition have relatively isotropic motion. The greatest vibrational amplitudes and anisotropy of motion appear in the carbonyl groups, indicating that the reported bond lengths in this paper have been shortened due to vibrational motion. These results are visible in the stereo-pair drawing in Figure 1.

The mean of 18 C–H bond lengths is 0.98 A with a mean deviation of 0.05 A. The only anomalous deviation from the average (−0.2 A) was for the C(19)–H-(19) bond in the phenyl group. This is not unexpected in view of the highly anisotropic thermal correction applied to C(19).