(IV) because of the inductive effects of the substituent electronegative atoms and hetero ring atoms. It is possible therefore that in these structures the stronger than usual attractive forces between $C^{\delta+}=O^{\delta-}$ dipoles are sufficiently powerful to influence the arrangement of molecules to bring carbonyl atoms closer together than London dispersion forces alone would allow. These forces would be dipole–dipole attraction (Keesom, 1921) and/or dipole-induced dipole attraction (Debye, 1920, 1921).

This suggestion agrees generally with the available observations. For instance the fact that the attraction of a $C^{\delta+}=O^{\delta-}$ dipole for a charge $(=C^{\delta+})$ is strongest along its axis will make the COC angle tend to 180 °C. This is about 160° in the reported cases. Also, on this basis the rather unusual arrangement in alloxan in which a ring carbon atom has close interactions with two oxygen atoms from opposite sides of the molecular plane (Fig. 4) is the expected result of the attraction of two $=O_6^{\delta-}$ for the same charge centre $=C_5^{\delta+}$. Perhaps the most puzzling thing about the close approach discussed here is that it has been observed in only four cases and not in compounds such as succinimide (Mason, 1956) and maleic anhydride (Marsh, Ubell & Wilcox, 1962) where there are non-hydrogen-bonded carbonyl groups. This is presumably because only in these four compounds is the $C^{\delta+}=O^{\delta-}$ dipole strong enough for interaction to occur.

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References

Biltz, H. (1912). *Ber. deutsch. chem. Ges.* **45**, 3659.
Bolton, W. (1936). *Acta Cryst.* **16**, 166.
Chu, S. C., Jeffrey, G. A. & Sakurai, T. (1962). *Acta Cryst.* **15**, 661.
Davies, D. R. & Blum, J. J. (1955). *Acta Cryst.* **8**, 129.
Debye, P. (1920). *Phys. Z.* **21**, 178.
Debye, P. (1921). *Phys. Z.* **22**, 302.
Hall, D. (1962). Unpublished work. The Crystallography Laboratory, The University of Pittsburgh, U.S.A.
Hassell, O. & Romming, C. (1962). *Quart. Rev. Chem. Soc. Lond.* **16**, No. 1, p. 1.
Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
Jeffrey, G. A., Ghose, S. & Warwicker, J. O. (1961). *Acta Cryst.* **14**, 881.
Keesom, W. H. (1921). *Phys. Z.* **22**, 129.
Marsh, R. E., Ubell, E. & Wilcox, H. E. (1962). *Acta Cryst.* **15**, 35.
Mason, R. (1956). *Acta Cryst.* **9**, 405.
Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
Shiono, R. (1962). Program No. 330, I.U.Cr. *World List of Crystallographic Computer Programs*, 1st edn.
Singh, C. (1960). *Acta Cryst.* **13**, 1036.
Stadler, H. P., Bolton, W. & Maitland, R. (1964). *Acta Cryst.* To be published.
Taylor, C. A. & Morley, K. A. (1959). *Acta Cryst.* **12**, 101.
Wallwork, S. C. (1961). *J. Chem. Soc.* pp. 98, 494.

Acta Cryst. (1964). **17**, 152

The Crystal Structure and Molecular Statics of Trindan, $C_{15}H_{18}$

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The crystal structure of trindan (tristrimethylenebenzene, $C_{15}H_{18}$) has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$ (C_{2h}^5) with

$$a=12{\cdot}67,\ b=5{\cdot}87,\ c=16{\cdot}92\ \text{Å};\ \beta=111°\ 41'.$$

The principle conclusions are that there is no significant alternation of bond lengths in the benzene ring, and the molecule is not completely coplanar. The static configuration of the molecule was computed from two different sets of force constants. The results indicate a preference for one of two sets of force constants for benzene.

Introduction

Over thirty years ago Mills & Nixon (1930) reported an interesting phenomenon involving the benzene ring. They observed that, by fusing saturated hydrocarbon rings of different sizes onto a benzene ring, it was possible in some cases to produce chemical behavior indicative (in their interpretation) of the double bonds being fixed in one of the two Kekulé structures. In the case of 5-hydroxyhydrindene (I) for example, the

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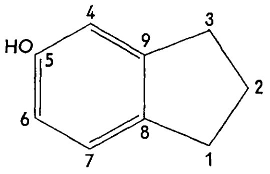

(I)

chemical evidence was interpreted as indicating fixation of the double bonds in the positions shown. It was pointed out by Sutton & Pauling (1935) that it is not reasonable, nor is it necessary for the explanation of the chemical evidence, to assume anything approaching such complete fixation. Should the presence of the five-membered ring cause one of the Kekulé structures to contribute a few per cent more than the other to the ground state of the molecule, an alternation of the double-bond character of the bonds could result with only relatively small changes in the bond lengths. This could conceivably produce chemical effects. A considerable amount of chemical work has been done in connection with the Mills–Nixon effect, and the reader is referred to a discussion of it by Hückel (1958). For a number of reasons, most modern workers in the field consider Mills & Nixon's original explanation to be obsolete.

However, the question of distortions in systems of this type still remains. The possible effect on the bond-lengths in the benzene ring is only one aspect of this problem. The coplanarity (or lack of it) and distribution of angular strain in a five-membered ring fused to a benzene ring are also of interest. To study these questions, we have determined the crystal structure of trindan (tristrimethylenebenzene, $C_{15}H_{18}$), in which three five-membered rings are placed symmetrically around a benzene ring (Fig. 1). One would expect that the effects of the strain in the five-membered rings on the bond lengths in benzene would be maximized in this compound. Furthermore, as will be seen, the equivalent bonds in the molecule are not related by crystalline symmetry. This allows each bond to be measured independently, and the agreement within a group of equivalent bonds serves as an internal measure of accuracy.

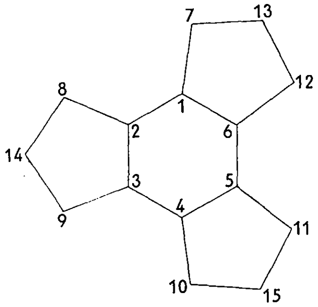

Fig. 1. Trindan molecule: numbering system used.

We have also computed the equilibrium static configuration of the trindan molecule from two possible sets of force constants. The experimental results indicate a preference for one of these sets.

Experimental

The prismatic crystals, which were prepared by a method described by Wallach (1897), were found to sublime slowly when exposed to the atmosphere. To arrest deterioration, the crystals were coated with a protective film by immersion in an aqueous solution of Aerosol. Weissenberg photographs were taken around the prism axis (b) and one perpendicular to it (c). The crystals were found to be monoclinic with lattice parameters

$$a=12\cdot67,\ b=5\cdot07,\ c=16\cdot92\ \text{Å};\ \beta=111^\circ\,41'\,.$$

Systematic absences indicated space group $P2_1/c$ (C_{2h}^5), and the calculated density of 1·126 g.cm^{-3}, for four molecules per unit cell, agrees well with the observed value of 1·141 g.cm^{-3} reported by Ziegler & Ditzel (1929).

Intensities were determined by the visual technique from multiple-film Weissenberg photographs (Cu $K\alpha$ radiation) of layer lines zero through four around b, and zero through nine around c. Very large thermal motion was apparent, as no reflections with $\sin\theta$ greater than 0·7 were observed. The intensities were converted to relative structure factors by appropriate corrections for Lorentz and polarization factors. Of the total of 316 different reflections measured, 195 were observed with both crystals. A least-squares procedure was used to convert the structure factors on the various film sets to a common relative scale, and only one scale factor was carried through the structure determination.

Structure determination

A Patterson projection along b was computed and its solution accomplished by employing a molecular model of trindan (Fig. 1). In a model of trindan twice its normal size (referred to the scale of the Patterson function), points were placed at the centers of the line segments connecting each pair of atoms. It is easy to show that the resulting distribution of points corresponds to the set of Patterson peaks arising from vectors between a pair of molecules related by a center of symmetry (or by a 2_1 axis in the projection). These peaks are found centered at $2\mathbf{r}_0$, in which $\mathbf{r}_0$ is the vector from a symmetry center (origin) to the molecular center. While the molecular center can, in general, be chosen arbitrarily, it is natural in this case to select the center of the benzene ring.

The above procedure showed that high densities of interatomic vectors occur at the molecular center and at the approximate midpoints of the benzene bonds (on the doubled scale). Fig. 2 shows the proposed

Table 1. *Atomic parameters for trindan*

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$
1	0·1869	0·0599	0·1743	0·0015	0·0034	0·0012	7·81	0·51
2	0·1798	0·9314	0·1037	0·0014	0·0032	0·0011	7·31	0·48
3	0·2536	0·9861	0·0619	0·0015	0·0032	0·0011	6·81	0·47
4	0·3323	0·1537	0·0898	0·0016	0·0032	0·0011	7·05	0·45
5	0·3406	0·2824	0·1619	0·0015	0·0030	0·0011	7·00	0·50
6	0·2684	0·2255	0·2030	0·0016	0·0031	0·0012	6·75	0·50
7	0·1161	0·0240	0·2332	0·0015	0·0031	0·0012	8·82	0·51
8	0·0955	0·7443	0·0625	0·0018	0·0033	0·0012	9·78	0·58
9	0·2345	0·8362	0·9827	0·0017	0·0035	0·0012	9·20	0·56
10	0·4194	0·2333	0·0507	0·0018	0·0033	0·0012	8·62	0·59
11	0·4263	0·4672	0·1789	0·0016	0·0033	0·0011	9·09	0·54
12	0·2578	0·3465	0·2827	0·0016	0·0033	0·0011	9·10	0·54
13	0·1761	0·1892	0·3030	0·0018	0·0038	0·0013	12·71	0·63
14	0·1330	0·6755	0·9850	0·0017	0·0033	0·0012	10·13	0·59
15	0·4939	0·4078	0·1190	0·0016	0·0037	0·0012	10·01	0·58

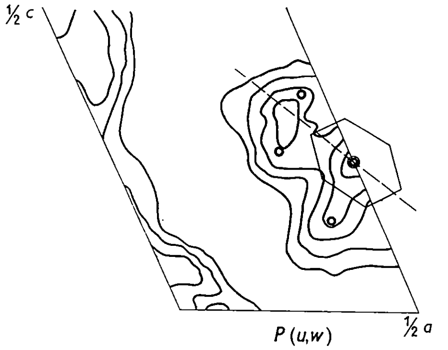

Fig. 2. Patterson projection $P(u, w)$ showing the orientation of the benzene ring, which is drawn to the same scale as the map. The multiple circles are placed at positions of high predicted density corresponding to this orientation.

relation of the benzene ring (normal scale) to the Patterson map. Thus, the coordinates of the molecular center were found to be $x=\frac{1}{4}$ and $z=\frac{1}{8}$, and the approximate orientation and axis of tilt (out of the x–z plane) were determined.

The angle of tilt of the molecule was deduced from the Patterson section $P(u, \frac{1}{2}, w)$. To do this, we note that all of the intramolecular interatomic distances occur in a plane (under the assumption of molecular planarity) which passes through the origin and intersects the plane $y=\frac{1}{2}$ at a distance $\frac{1}{2}c \cot \varphi$ (φ=angle of tilt) from the projection of the origin on this plane. This intersection was easily found as a strip of high density on $P(u, \frac{1}{2}, w)$. The orientation of the axis of tilt was also verified from the orientation of this strip.

From the orientation of the tilt axis, the angle of tilt, the coordinates of the molecular center, and the orientation of the molecule, the x and z coordinates of all of the carbon atoms were computed. These coordinates were refined by successive Fourier syntheses until no changes in the signs of significant structure factors occurred.

The y coordinate of the molecular center was found by an analytical procedure. The expression for the structure factor can be written

Table 2. *Bond distances in trindan*

Atoms	Distance	Average*	Standard deviation
2–3	1·402 Å	1·392 Å	0·016 Å
4–5	1·405		
6–1	1·370		
1–2	1·388	1·375	0·014
3–4	1·356		
5–6	1·380		
2–8	1·511	1·541	0·031
3–9	1·545		
4–10	1·553		
5–11	1·486		
6–12	1·573		
1–7	1·581		
8–14	1·603	1·565	0·041
14–9	1·607		
10–15	1·572		
15–11	1·590		
12–13	1·519		
13–7	1·500		

* Average of set related by the assumed symmetry (C_{3v}) of the isolated molecule.

Table 3. *Bond angles in trindan*

Atoms	Angles	Average*	Standard deviation
1–2–3	117·8°	120·0°	2·1°
2–3–4	122·2		
3–4–5	120·1		
4–5–6	117·2		
5–6–1	123·1		
6–1–2	119·5		
8–2–3	115·0	112·5	1·7
9–3–2	112·8		
10–4–5	111·8		
11–5–4	112·1		
12–6–1	109·5		
7–1–6	113·5		
2–8–14	100·8	101·5	1·3
3–9–14	100·6		
4–10–15	102·2		
5–11–15	104·1		
6–12–13	101·6		
1–7–13	99·8		
8–14–9	110·7	110·5	2·8
10–15–11	107·0		
12–13–7	113·8		

* See footnote, Table 2.

$$F_{hkl} = A_{hkl} \cos 2\pi k y_0 + B_{hkl} \sin 2\pi k y_0$$

in which y_0 is the coordinate of the molecular center, and A_{hkl} and B_{hkl} depend only on the (known) x and z coordinates of the fifteen atoms. The value of y_0 was chosen to give good agreement with a number of strong reflections. From this value, the y coordinates of the fifteen carbon atoms were computed.

The structure was refined in three dimensions by a single Fourier synthesis, a difference synthesis, and eight least-squares cycles in which individual isotropic temperature factors were used. The final value for $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ was 0·122 (observed magnitudes only), and this parameter changed by less than 0·001 in the last cycle. The final atomic parameters are given in Table 1. The bond distances and angles calculated from the final parameters are listed in Tables 2 and 3.

Accuracy of the structure

The r.m.s. errors in the atomic parameters are listed in Table 1. These are nearly the same for each of the fifteen carbon atoms, although there is a discernible tendency for the errors to increase with distance from the center of the molecule. That the errors are approximately isotropic is indicated by the fact that

$$a\sigma_x \sin\beta = 0{\cdot}019,\ b\sigma_y = 0{\cdot}019,\ c\sigma_z \sin\beta = 0{\cdot}018\ \text{Å}$$

in which the r.m.s. of the values listed in Table 1 were used for σ_x, σ_y, and σ_z. These numbers would be identical for the case of isotropic errors.* The standard error in the carbon-carbon distances is $0{\cdot}019 \times \sqrt{2} = 0{\cdot}027$ Å.

The standard deviations from the mean of sets of carbon–carbon distances related by assumed molecular symmetry C_{3v} is given in Table 2. The weighted r.m.s. value of these deviations is 0·026 Å, which is in good agreement with the number computed above from the observed and calculated structure factors. The figures in Table 2 indicate an appreciable decrease in accuracy with increase in distance from the center of the molecule.

We conclude that there is no significant alteration of bond lengths from their normal values of 1·39 Å (benzene) and 1·54 Å (single bond). In particular, there is no significant alteration of bond lengths around the benzene ring.

The standard error (in degrees) in a bond angle φ with sides l_1 and l_2 is given by

$$\sigma_\varphi = \sigma_d \left(\frac{2}{l_1^2} + \frac{2}{l_2^2} - \frac{2\cos\varphi}{l_1 l_2} \right)^{\frac{1}{2}} \left(\frac{180}{\pi} \right), \qquad (1)$$

in which the (isotropic) r.m.s. displacement in a given direction $\sigma_d = 0{\cdot}019$ Å, as indicated above. This varies from 1·5 to 1·8 degrees for the angles listed in Table 3, and has an overall r.m.s. value of 1·6°. The overall r.m.s. deviation between columns 2 and 3 of Table 3 is 1·9°. Again, it does not appear that there are significant differences between chemically identical bond angles. On the other hand, the deviations of the angles listed in column 3 of Table 3 from each other and from their 'unstrained' values are highly significant, and will be interpreted in a later section.

Thermal motion

It is obvious that the accuracy of this determination is considerably less than is usually obtained with structures of this type. This is due to the large thermal motion, which is apparent from examination of column 8 of Table 1. The mean value of B is 8·68 Å^2, which corresponds to an overall r.m.s. atomic displacement of 0·33 Å.

There are three types of carbon atom in the trindan molecule, atoms 1–6, 7–12, and 13–15, in order of increasing distance from the molecular center. It is obvious that there is no significant variation among B's of atoms of the same type, but there is a large and significant increase of B with increasing distance from the molecular center. In fact, the equation (determined by least-squares),

$$B = 6{\cdot}40 + 0{\cdot}34R^2\,, \qquad (2)$$

in which R is the distance from the molecular center, reproduces the observed average B values within experimental error. The implication is very strong that the thermal motion is due mostly to translational and oscillational vibrations, and this is what one would expect in the case of thermal motion of this magnitude at room temperature. The corresponding r.m.s. translational and oscillational displacements are

$$\sqrt{(\overline{u^2})} = \sqrt{(6{\cdot}40/8\pi^2)} = 0{\cdot}28\ \text{Å}\,,$$
$$\sqrt{(\overline{\theta^2})} = (180/\pi)\sqrt{(0{\cdot}34/8\pi^2)} = 3{\cdot}7^\circ\,.$$

Since the oscillational motions are normal to the radius vector from the center of the molecule, they give rise to an apparent contraction of the molecule when the mean atomic positions are used to calculate the geometrical parameters (Cruickshank, 1956). The correction factor to be applied to intramolecular distances is $1 + 0{\cdot}34/16\pi^2 = 1{\cdot}0022$. This would increase all C–C bond distances by 0·003 Å, an insignificant correction, and there is no effect on the bond angles.

Planarity of the molecule

The least-squares (Schomaker, Waser, Marsh & Bergman, 1959) plane, determined from the coordinates of atoms 1–12 in the molecule nearest the origin, has the equation

$$3{\cdot}1214x - 1{\cdot}9216y + 3{\cdot}0068z = 1\,, \qquad (3)$$

and this plane is 1·994 Å from the origin. The distances

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* They could be the same for highly anisotropic errors, but this would be improbable.

of the fifteen carbon atoms from this plane are given in Table 4. It is evident that we may regard the benzene ring and the methylene carbon atoms adjacent to it as being essentially coplanar, although the displacement of C(11) from the mean plane is statistically significant. On the other hand, the displacements of C(13) and C(15) from the mean plane of the rest of the molecule are quite large. This is consistent with the non-planar cyclopentane molecule, as discussed by Kilpatrick, Pitzer & Spitzer (1947). As in the case of cyclopentane, this distortion from the planar structure is probably due to hydrogen repulsions.

Table 4. *Distances of atoms from mean plane*

The positive sign indicates that the atom is on the side of the plane opposite the origin.

Atom no.	Distance	r.m.s. distance
1	−0·015 Å	0·019 Å
2	+0·011	
3	+0·009	
4	+0·024	
5	+0·015	
6	+0·031	
7	+0·036	0·036
8	−0·045	
9	−0·010	
10	+0·026	
11	−0·058	
12	−0·021	
13	+0·195	0·175
14	−0·013	
15	+0·231	

It seems rather strange that C(14) lies (within experimental error) in the mean plane, instead of being displaced from it by about 0·2 Å, as are the chemically equivalent atom C(13) and C(15). We considered the possibility that the position found in the structure determination might be the mean position in a disordered structure in which C(14) is randomly located on either side of the mean plane. However, a careful examination of a three-dimensional difference Fourier map failed to reveal any evidence for such behavior; furthermore, the temperature factor for this atom is not abnormal.

We conclude that the potential function concerned with the displacement of these atoms out of the plane is rather flat in the vicinity of the plane, and the actual positions of the atoms are determined, at least in part, by packing considerations.

Static treatment of the molecule

To compute the static configuration of the molecule from the molecular potential function, we assume first of all that the molecule is planar. This may seem to be a rather drastic assumption in view of the appreciable non-planarity discussed in the previous section. However, the sums of the angles in the three five-membered rings are 538·2°, 539·9°, and 537·2°. If the distortions due to non-planarity were distributed equally among the ring angles, the largest distortion would be 0·6°, and the overall average 0·3°. These are considerably less than the errors in the determination of the angles, and are very likely smaller than the errors in the static calculation arising from uncertainties in the force constants.

The configuration of the molecule will be expressed in terms of the deviations of the interatomic distances and angles from their normal values — the values they would presumably have in an unstrained molecule. The nomenclature is given in Fig. 3. The potential function used in this treatment is

$$\begin{aligned}2V=\sum_{i=1}^{6}\{&F_t^1t_i^2+2F_t^2t_it_{i+1}+2F_t^3t_it_{i+2}+F_t^4t_it_{i+3}+F_\beta^1\beta_i^2\\&+2F_\beta^2\beta_i\beta_{i+1}+2F_\beta^3\beta_i\beta_{i+2}+F_\beta^4\beta_i\beta_{i+3}+2F_{t\beta}^1(t_i\beta_i-t_i\beta_{i+1})\\&+2F_{t\beta}^2(t_i\beta_{i+2}-t_i\beta_{i+5})+2F_{t\beta}^3(t_i\beta_{i+3}-t_i\beta_{i+4})\\&+k_1(s_i^2+r_i^2)+k_2\gamma_i^2\}+\sum_{i=1}^{3}k_2\delta_i^2\end{aligned}\tag{4}$$

in which it is understood that the result of addition of the subscripts is reduced to the corresponding congruent number (modulo 6) less than 7. In this function, all of the interaction terms have been neglected except those involved in the benzene ring and its external angles. The interior benzene angles are not included since they are required by symmetry to be 120°.

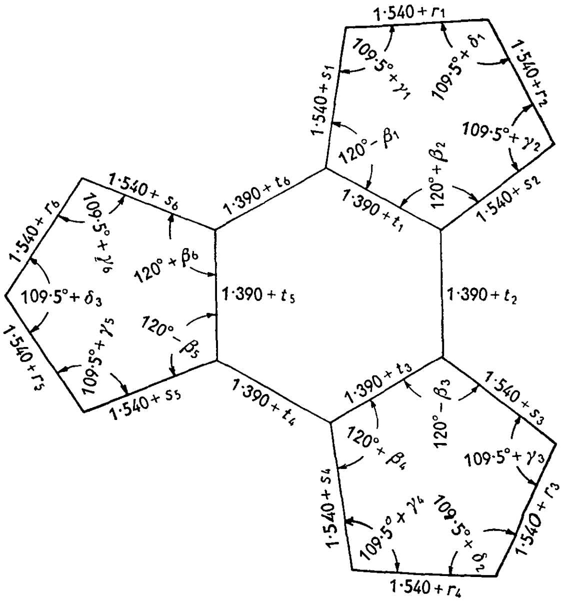

Fig. 3. Parameters used in discussing the static configuration of trindan.

We now assume that the point symmetry of the static molecule is D_{3h}. The potential function then reduces to

$$\begin{aligned}2V=3f_1(t_1^2+t_2^2)+6f_2t_1t_2+6f_3\beta_1^2+6f_4(t_1\beta_1-t_2\beta_1)\\ +6k_1(s_1^2+r_1^2)+3k_2(2\gamma_1^2+\delta_1^2)\ ,\end{aligned}\tag{5}$$

in which

$$\begin{aligned}f_1&=F_t^1+2F_t^3=\tfrac{1}{2}[F_{tt}(A_{1g})+F_{tt}(B_{2u})]\ ,\\ f_2&=2F_t^2+F_t^4=\tfrac{1}{2}[F_{tt}(A_{1g})-F_{tt}(B_{2u})]\ ,\\ f_3&=F_\beta^1-2F_\beta^2+2F_\beta^3-F_\beta^4=F_{\beta\beta}(B_{2u})\ ,\\ f_4&=2(F_{t\beta}^1+F_{t\beta}^2-F_{t\beta}^3)=F_{t\beta}(B_{2u})\ ,\\ F_{tt}(A_{1g})&=F_t^1+2F_t^2+2F_t^3+F_t^4\ ,\\ F_{tt}(B_{2u})&=F_t^1-2F_t^2+2F_t^3-F_t^4\ .\end{aligned}\tag{6}$$

The constants $F_{tt}(A_{1g})$, $F_{tt}(B_{2u})$, $F_{\beta\beta}(B_{2u})$, and $F_{t\beta}(B_{2u})$ are those associated with the corresponding symmetry coordinates of benzene (Wilson, Decius & Cross, 1955). Only the A_{1g} and B_{2u} coordinates maintain D_{3h} symmetry.

Since there are only five independent parameters in the trindan skeleton of symmetry D_{3h}, there must be two independent necessary relations among the seven coordinates which appear in (5). The first of these can be taken to be the condition that the five-membered ring has a plane of symmetry:

$$\begin{aligned}\tfrac{1}{2}(1\cdot 390+t_1)=(1\cdot 540+r_1)\sin\,(0.9553+\tfrac{1}{2}\delta_1)\\ -(1\cdot 540+s_1)\sin\,(\tfrac{1}{6}\pi-\beta_1)\ .\end{aligned}\tag{7}$$

When this is expanded, and only the linear terms in r_1, s_1, t_1, β_1, and δ_1 are kept, it becomes

$$-\tfrac{1}{2}t_1-\tfrac{1}{2}s_1+0\cdot 8165r_1+1\cdot 3337\beta_1+0\cdot 4446\delta_1=0\cdot 2076\ .\tag{8}$$

The other condition can be the requirement that the sum of the angles in the five-membered ring is 3π. In terms of our parameters, this becomes

$$2\beta_1-2\gamma_1-\delta_1=0\cdot 4958\tag{9}$$

The equilibrium static configuration is then obtained by minimizing V subject to conditions (8) and (9). The solution is

$$\begin{aligned}t_1&=(1/\mathrm{D})[\lambda_1(\tfrac{1}{2}f_1f_3+0\cdot 6669f_1f_4+0\cdot 6669f_2f_4-\tfrac{1}{4}f_4^2)\\ &\quad+\lambda_2(f_1f_4+f_2f_4)]\ ,\\ t_2&=(1/\mathrm{D})[\lambda_1(-0\cdot 6669f_1f_4-\tfrac{1}{2}f_2f_3-0\cdot 6669f_2f_4-\tfrac{1}{4}f_4^2)\\ &\quad+\lambda_2(-f_1f_4-f_2f_4)]\ ,\\ s_1&=\lambda_1/8k_1\ ,\\ r_1&=-0\cdot 2041\lambda_1/k_1\ ,\\ \beta_1&=(1/\mathrm{D})[\lambda_1(-0\cdot 6669f_1^2-\tfrac{1}{4}f_1f_4+0\cdot 6669f_2^2-\tfrac{1}{4}f_2f_4)\\ &\quad+\lambda_2(-f_1^2+f_2^2)]\ ,\\ \gamma_1&=\tfrac{1}{2}\lambda_2/k_2\ ,\\ \delta_1&=(-0\cdot 2223\lambda_1+\tfrac{1}{2}\lambda_2)/k_2\ ,\end{aligned}\tag{10}$$

in which λ_1 and λ_2 are Lagrangian multipliers determined by the equations

$$\begin{aligned}&\lambda_1[(1/\mathrm{D})(-0\cdot 8894f_1^2-\tfrac{1}{4}f_1f_3-0\cdot 6669f_1f_4+0\cdot 8894f_2^2\\ &\quad-0\cdot 6669f_2f_4+\tfrac{1}{8}f_4^2)-0\cdot 2282/k_1-0\cdot 0988/k_2]\\ &\quad+\lambda_2[(1/\mathrm{D})(-1\cdot 3337f_1^2-\tfrac{1}{2}f_1f_4+1\cdot 3337f_2^2-\tfrac{1}{2}f_2f_4)\\ &\quad+0\cdot 2223/k_2]=0\cdot 2076\\ &\lambda_1[(1/\mathrm{D})(-1\cdot 3337f_1^2-\tfrac{1}{2}f_1f_4+1\cdot 3337f_2^2-\tfrac{1}{2}f_2f_4)\\ &\quad+0\cdot 2223/k_2]+\lambda_2[(2/\mathrm{D})(-f_1^2+f_2^2)-3/2k_2]=0\cdot 4958\ .\end{aligned}\tag{11}$$

In these equations

$$D=2(f_1^2f_3-f_1f_4^2-f_2^2f_3-f_2f_4^2)\ .$$

To obtain numerical results, two sets of force constants were used. In both of these, we took the aliphatic C–C stretch- and C–C–C bending constants to be

$$k_1=4\cdot 5\ \mathrm{md.\AA^{-1}}\ \text{(Herzberg,1945)}\ ,$$
$$k_2=0\cdot 85\ \mathrm{md.\AA}\ \text{(Pitzer, 1940)}\ .$$

The remaining constants were obtained from a calculation of the symmetry force constants from the spectra of benzene and its deuterium derivatives by Crawford & Miller (1949). Two sets of roots were obtained by these workers, and we have computed the parameters from (10) for each of these. The numerical values are given in Table 5.

There is no reason to doubt that the force constants involved in stretching the ring bonds in benzene are essentially the same as the corresponding constants in trindan. On the other hand, one might expect some change in the force constants involved in bending the external benzene angles when the ligands are changed from hydrogen to carbon. However, different orders of magnitude or a change in sign of the interaction constant are not expected.

Table 5. *Force constants used to calculate static configuration of trindan*

Constant*	Set 1	Set 2
$f_1=\frac{1}{2}(\Lambda_1+\Lambda_2)$	7·278 md.Å^{-1}	6·411 md.Å^{-1}
$f_2=\frac{1}{2}(\Lambda_1-\Lambda_2)$	0·554 md.Å^{-1}	1·422 md.Å^{-1}
$f_3=r^2{}_{\mathrm{C-H}}\Gamma_2$	1·108 md.Å	1·107 md.Å
$f_4=r_{\mathrm{C-H}}\mu_2$	1·403 md	−0·219 md

* The Greek letters are the nomenclature of Crawford & Miller (1949), who used constants with units of md.Å^{-1}. We used $r_{\mathrm{C-H}}=1\cdot 08$ Å.

The results of the static calculation are compared with the experimental measurements in Table 6.

The experimental parameters in Table 6 are the mean values given in Tables 2 and 3, increased in the case of bond lengths by the 0·003 Å correction arising from the molecular oscillation. There are small errors in the calculation arising from the expansion of (7) to obtain (8). While these could be eliminated by another iteration, there is little to be gained by doing this since these errors are small compared with the errors due to uncertainties in the force constants and failure of the harmonic force law for these relatively

Table 6. *Comparison of observed and calculated molecular parameters of trindan*

		Calculated		Deviation	
Parameter	Experimental*	Set 1	Set 2	Set 1	Set 2
$1{\cdot}390+t_1$	1·395 ± 0·011 Å	1·356 Å	1·385 Å	0·039 Å	0·010 Å
$1{\cdot}390+t_2$	1·378 ± 0·010	1·421	1·386	−0·043	−0·008
$1{\cdot}540+s_1$	1·544 ± 0·014	1·536	1·532	0·008	0·012
$1{\cdot}540+r_1$	1·568 ± 0·018	1·547	1·552	0·021	0·016
$120^\circ-\beta_1$	112·5 ± 0·8°	111·4°	111·4°	1·1°	1·1°
$109{\cdot}5^\circ+\gamma_1$	101·5 ± 0·6	105·0	104·4	−3·5	−2·9
$109{\cdot}5^\circ+\delta_1$	110·5 ± 2·0	107·3	108·5	3·2	2·0

* The precisions quoted here were computed from the r.m.s. deviations from the means of the three or six measurements of the corresponding parameter.

large deviations from the unstrained angles. The total strain energies are 10·6 and 14·2 kcal.mole^{-1} for sets 1 and 2, respectively. These are probably low since the energy arising from hydrogen repulsion has not been included.

Crawford & Miller's set 1 would predict considerable alternation of bond lengths around the benzene ring, although in the opposite direction to that suggested by the Mills–Nixon effect. This is clearly due to the large value of the angle–bond interaction constant which they called μ_2. The fact that no such alternation was found provides a basis for preferring their set 2. Coulson & Longuet-Higgins (1948) have used the empirical LCAO method to compute the bond-stretching force constant of benzene, and they calculate $F_t^1=6{\cdot}84$, $F_t^2=1{\cdot}14$, $F_t^3=0{\cdot}73$, and $F_t^4=$ 0·52 md.Å^{-1}. This gives $f_1=5{\cdot}38$ and $f_2=2{\cdot}80$ md.Å^{-1}. This also is in better agreement with set 2, although the agreement is not particularly good.

Longuet-Higgins & Coulson (1946) have computed the static configuration of hydrindene. Their angular strains in the five-membered ring are quite close to our computed ones in Table 6. They compute a compression in the benzene bond which is shared with the five-membered ring of 0·022 Å, which is considerably larger than the 0·005 Å we compute with the set-2 force constants. This is partly due to the fact that they did not include an angle-bond interaction constant, which tends to elongate this bond when it is negative.

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References

Coulson, C. A. & Longuet-Higgins, H. C. (1948). *Proc. Roy. Soc.* A, **193**, 456.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 757.

Crawford, B. L. & Miller, F. A. (1949). *J. Chem. Phys.* **17**, 249.

Herzberg, G. (1945). *Infrared and Raman Spectra of Polyatomic Molecules.* New York: Van Nostrand.

Hückel, W. (1958). *Theoretical Principles of Organic Chemistry*, pp. 809–817. Amsterdam: Elsevier.

Kilpatrick, J. E., Pitzer, K. S. & Spitzer, R. (1947). *J. Amer. Chem. Soc.* **69**, 2483.

Longuet-Higgins, H. C. & Coulson, C. A. (1946). *Trans. Faraday Soc.* **42**, 756.

Mills, W. H. & Nixon, I. G. (1930). *J. Chem. Soc.*, p. 2510.

Pitzer, K. S. (1940). *Chem. Rev.* **27**, 39.

Schomaker, V., Waser, J., Marsh, R. E. & Bergman, G. (1959). *Acta Cryst.* **12**, 600.

Sutton, L. E. & Pauling, L. (1935). *Trans. Faraday Soc.* **31**, 939.

Wallach, O. (1897). *Ber. dtsch. chem. Ges.* **30**, 1094.

Wilson, E. B., Decius, J. C. & Cross, P. C. (1955). *Molecular Vibrations*, Chapter 10. New York: McGraw-Hill.

Ziegler, K. & Ditzel, F. (1929). *Liebigs Ann.* **473**, 194.