Acta Cryst. (1965). **19**, 235

The Crystal Structure of [18]annulene. II. Results

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(*Received* 27 *October* 1964)

The X-ray analysis of [18]annulene has shown that the molecule contains two kinds of C–C bond: twelve inner bonds of mean length 1·382 ± 0·003 Å, and six outer bonds of 1·419 ± 0·004 Å. The molecule is non-planar, with carbon atoms displaced from the mean plane by up to 0·085 Å, evidently because of non-bonded interactions between neighboring internal C–H groups. The molecular configuration is close to one of $\bar{3}$ symmetry. It is not clear whether the failure to adopt $\bar{3}m$ symmetry is due to crystal forces. The same intramolecular repulsions that cause the out-of-plane deformation must contribute to, but cannot fully account for, the variation in bond lengths. This variation does not appear to have a single simple explanation.

The observed molecular structure rules out the bond-alternation hypothesis that has been proposed as an explanation for the ultraviolet absorption and for the nuclear magnetic resonance spectrum.

Molecular symmetry

The X-ray study reported in part I (the preceding paper) has disclosed a quite unexpected molecular structure for [18]annulene. With regard to their lengths the C–C bonds are of two kinds: the twelve inner bonds, *e.g.* C(1)–C(2) and C(3)–C(4), of mean length $r_I = 1{\cdot}382$ Å, and the six outer bonds, *e.g.* C(2)–C(3), of mean length $r_O = 1{\cdot}419$ Å. The C–C–C bond angles similarly fall into two classes, averaging 127·52° for the six external angles (between pairs of inner C–C bonds), and 123·83° for the twelve internal angles (between inner and outer C–C bonds). The C–H bond lengths are reasonably uniform, in view of their large experimental uncertainties, averaging 1·01 Å and 1·00 Å for the internal and external bonds, respectively.

If we suppose that there are, in fact, only two chemically distinct kinds of C–C bond in the molecule, the scatter of the observed bond lengths provides an independent estimate of the experimental coordinate accuracy. In contrast to the least-squares estimate (part I, equation 2), which allows primarily for random observational errors (and somewhat underestimates even these because of the neglect of off-diagonal matrix elements), this 'bond-scatter' estimate may include the effects of some systematic errors and of any bond-length variation due to crystal forces. This estimate, with proper allowance for the correlation between pairs of adjacent inner bonds having an atom in common, gives for the nine experimental bond lengths

$$\sigma(r) = 0{\cdot}0077 \text{ Å},$$

corresponding to standard deviations for the means of the inner and outer bond lengths respectively equal to

$$\sigma(r_I) = 0{\cdot}0032, \quad \sigma(r_O) = 0{\cdot}0044 \text{ Å}.$$

These figures imply an average standard deviation in atomic coordinates ~ 0·0054 Å. This is appreciably higher than the largest of the average coordinate errors derived from the least-squares estimate (part I, Table 4).

Even in relation to the more conservative 'bond-scatter' estimate, the difference of 0·037 Å between r_I and r_O is highly significant; possible reasons for this difference are considered below.

In the crystal the molecule has symmetry $\bar{1}$ but deviates only slightly from symmetry $\bar{3}$. It is virtually certain that, in isolation, the molecule would have at least $\bar{3}$ symmetry. Applying the covering operations of point group $\bar{3}$ to the observed atomic positions, we obtain three almost coincident images of the molecule. From these we can derive mean atomic positions conforming exactly to $\bar{3}$ symmetry. The r.m.s. displacements, along the molecular axes (part I, Table 3), of the observed atomic positions from the respective mean positions are:

$$\Delta L = 0{\cdot}0211, \quad \Delta M = 0{\cdot}0212, \quad \Delta N = 0{\cdot}0098 \text{ Å}.$$

There can be no doubt of the experimental significance of these displacements, even if the r.m.s. coordinate error is taken as 0·0054 Å, as given by the 'bond-scatter' estimate. The deformation, which we attribute to crystal forces, has primarily the form of an elongation of the molecule along *L*, and a compression along *M*, as may be seen in Fig. 1.

The shorter intermolecular contact distances are listed in Table 1. Two carbon atoms of molecule *F* (Fig. 1) make close contact, at 2·83 and 2·85 Å, with atom H(9′). Repulsion at these short separations, acting against equal and opposite forces at H(9), must account for the compression of the molecule along its *M* axis. These repulsions evidently exceed the force between H(3) and H(*G*3′), which is without obvious effect on the molecular shape.

In the absence of any intermolecular forces the molecular symmetry might be even higher than $\bar{3}$. Only in the out-of-plane coordinates does the observed configuration depart appreciably from one of symmetry $\bar{3}m$. If, in the isolated molecule, out-of-plane deformation stems only from repulsions between adjacent internal C–H groups, we should expect $\bar{3}m$ symmetry, since these intramolecular repulsions would not preclude symmetry planes passing through the $\bar{3}$ axis and through atoms C(1) and H(1), or C(4) and H(4), or C(7) and H(7), respectively. On the other hand, it seems unlikely *a priori* that intermolecular contacts in a monoclinic crystal would have just the symmetrical disposition required to destroy such mirror planes and yet so nearly preserve the $\bar{3}$ inversion axis. Nevertheless, examina-

Table 1. *Intermolecular contact distances* (Å) *between a reference molecule, centered at the origin, and its neighbors, identified by letter as in Fig.* 1.

The first-designated atom of each pair belongs to the reference molecule and has the coordinates *x*, *y*, *z* listed in part I, Table 2. The contacting atoms in the several neighboring molecules have coordinates related as indicated to those in the cited Table. All symmetry-independent *C* ··· C distances under 3·6 Å, C ··· H distances under 3·2 Å, and H ··· H distances under 2·8 Å are listed.

To molecule *B* at $(x, 1+y, z)$:					
C(6) ··· C(3)	3·317	C(4) ··· H(2)	3·18		
C(8) ··· C(4)	3·379	H(4) ··· C(2)	3·19		
C(7) ··· C(4)	3·417				
C(7) ··· C(3)	3·437				
C(4) ··· C(2)	3·532				
C(6) ··· C(4)	3·567				
C(5) ··· C(3)	3·583				
To molecule *C* at $(x, y, 1+z)$:					
		C(3) ··· H(5′)	3·16		
To molecule *D* at $(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$:					
		C(6) ··· H(6)	3·08	H(6) ··· H(8)	2·49
		C(6) ··· H(8)	3·20		
To molecule *E* at $(-\frac{1}{2}-x, \frac{1}{2}+y, -z)$:					
		C(2) ··· H(9′)	2·83		
		C(1) ··· H(9′)	2·85		
		C(9′) ··· H(9′)	3·02		
		C(8′) ··· H(2)	3·05		
To molecule *G* at $(x, -1+y, 1+z)$:					
		C(3) ··· H(3′)	3·13	H(3) ··· H(3′)	2·25

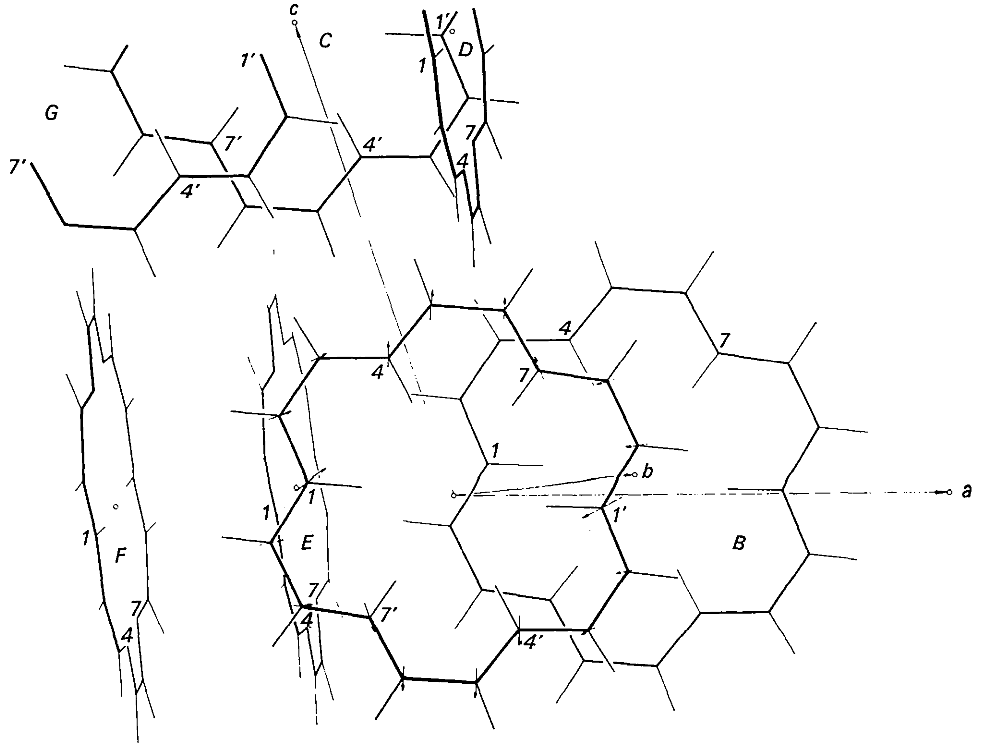

Fig. 1. Environment of reference molecule, centered at origin, projected onto mean molecular plane. Arrows through carbon positions show deviations from $\bar{3}$ symmetry, exaggerated ten times. Neighboring molecules are identified, by letter, in Table 1, except molecule *F* at $(-\frac{1}{2}-x, -\frac{1}{2}+y, -z)$.

Table 2(*a*). *Observed and calculated components of the atomic vibration tensors, in* Å², *referred to molecular axes L, M, N*

	10^4V_{11}		10^4V_{22}		10^4V_{33}		10^4V_{12}		10^4V_{23}		10^4V_{13}	
Atom	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
C(1)	247	239	336	327	256	273	24	31	−95	−100	10	6
C(2)	295	270	397	360	233	260	88	84	−116	−103	−34	2
C(3)	196	213	393	420	278	256	98	99	−106	−105	−16	4
C(4)	161	156	430	414	297	267	44	52	−113	−103	13	8
C(5)	126	143	497	493	261	268	29	25	−82	−104	13	9
C(6)	157	160	442	474	257	278	−41	−35	−62	−102	−1	11
C(7)	178	181	416	388	270	282	−43	−33	−112	− 99	17	10
C(8)	241	258	350	372	314	284	−43	−58	−113	−97	35	7
C(9)	319	299	315	330	281	277	−6	−14	−110	−98	25	5

tion of the closer van der Waals contacts shows that such an arrangement cannot be ruled out.

The shortest intermolecular carbon–carbon separation is 3·317 Å between atoms C(6) and C(*B*3) of parallel molecules related by the [010] translation (Table 1 and Fig. 1). A repulsive interaction between these two atoms would produce a negative displacement of C(3) and a positive displacement of C(6) from the mean molecular plane. Such displacements are, indeed, observed. However, atom C(9) is slightly further displaced from the plane than either C(3) or C(6). This may, perhaps, be associated with the short H(9′) · · · C(*F*1) and H(9′) · · · C(*F*2) contacts, which have been blamed for the in-plane distortion of the molecule. The symmetry-related contacts at H(9) lie nearly in-plane but they both have small out-of-plane components whose sense is consistent with the observed negative displacement of C(9). We should expect, however, that if these repulsions can cause such a large out-of-plane displacement of C(9) and H(9) they ought to produce even greater effects at C(1) and C(2), where they act in a direction nearly normal to the mean plane. No such effects are observed, but it may be argued that the forces on these carbon atoms have less leverage than those acting on the exocyclic hydrogen atom and, further, that because the force is shared by two carbon atoms its effects are too diffuse to be clearly evident.

Thus, the directions of the important intermolecular contacts permit the conclusion that, provided the associated forces were of suitable magnitude (see below), these contacts could account for the loss of the expected three mirror planes. In the absence of a more plausible explanation one would like to suppose that the isolated molecule has $\bar{3}m$ symmetry, with atoms C(2), C(3), C(5), C(6), C(8), and C(9) close to the mean plane, but that the symmetry is lowered in the crystal to very near $\bar{3}$.

Thermal motions

On the assumption that the thermal vibrations of the atoms consist mainly of rigid-body motions of the molecule, it is possible to analyse these anisotropic motions in terms of the symmetric tensors, **T**, giving the translational vibrations of the mass center, and **ω**, giving the librational oscillations of the molecule about axes through its center (Cruickshank, 1956). This analysis has been performed in the molecular coordinate system defined by the inertial axes *L*, *M*, and *N*.

Table 2(*b*). *Mean square thermal displacements* (Å²) *of hydrogen atoms*

Atom	$10^3\overline{u^2}$	Atom	$10^3\overline{u^2}$	Atom	$10^3\overline{u^2}$
H(1)	22	H(4)	−1	H(7)	4
H(2)	11	H(5)	7	H(8)	14
H(3)	−7	H(6)	4	H(9)	11

From the thermal parameters β_{ij} of each of the nine carbon atoms, we computed the components V_{ij} of the atomic vibration tensor in the molecular coordinate system. Table 2(*a*) lists, in columns headed 'obs', the six independent V_{ij} for each atom. Cruickshank's (1956) least-squares procedure was used to determine the components of **T** and **ω** and their estimated standard deviations (Table 3).

Table 3. *Components of rigid-body molecular vibration tensors* **T** (Å²) *and* **ω** (rad²) *and their estimated standard deviations, referred to molecular axes L, M, N.*

$$10^4\,\mathbf{T} = \begin{pmatrix} 142 & 17 & 10 \\ & 324 & -99 \\ & & 280 \end{pmatrix} \pm \begin{pmatrix} 6 & 5 & 7 \\ & 6 & 7 \\ & & 23 \end{pmatrix}$$

$$10^5\,\boldsymbol{\omega} = \begin{pmatrix} -6 & -10 & 5 \\ & -8 & 4 \\ & & 116 \end{pmatrix} \pm \begin{pmatrix} 20 & 5 & 7 \\ & 20 & 7 \\ & & 6 \end{pmatrix}$$

By comparing the values of V_{ij} calculated from **T** and **ω** (listed in Table 2(*a*) in columns headed 'calc') with the corresponding observed values, we confirm that the hypothesis of rigid-body motion is correct within the experimental error. From the r.m.s. value (0·0018 Å²) of the difference V_{ij} (obs) − V_{ij} (calc), an estimate of $\sigma(V_{ij}) \sim [54/(54-12)]^{\frac{1}{2}} \times 0{\cdot}0018 = 0{\cdot}0020$ Å² can be derived, allowing for the fact that 12 parameters T_{ij} and ω_{ij} were determined from $9 \times 6 = 54$ independent V_{ij}. The value of $\sigma(V_{ij})$ thus estimated lies within the range of the several average $\sigma(U'_{ii})$ values listed in part I, Table 4. We have verified also that the discrepancies **V**(obs) − **V**(calc) show no evidence of the molecular symmetry that would be expected if they were due to internal vibrations, or to bonding anisotropy, or to (static or dynamic) packing disorder of non-centrosymmetric molecules.

The translational motion of the molecule is anisotropic, with the largest component near the direction of the short (4·8 Å) crystal axis. It appears that neighboring planar molecules making 'face-to-face' contact vibrate more readily against each other than against differently oriented neighbors (Lonsdale, 1961*b*). Similar behaviour has been found in thioacetamide (Truter, 1959), diketopiperazine (Lonsdale, 1961*a*, *b*), *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961), sodium tropolonate (Shiono, 1961), benzo[*c*]phenanthrene and 1,12-dimethylbenzo[*c*]phenanthrene (Hirshfeld, Sandler & Schmidt, 1963), 2,5-dimethylquinone and duroquinone (Hirshfeld & Rabinovich, to be published).

The librational motion is small and consists almost entirely of oscillation about the normal to the mean molecular plane. This is evident from the fact that all components of $\boldsymbol{\omega}$ except ω_{33} are small in comparison with their standard deviations However, the accuracy of ω_{11}, ω_{22}, and T_{33} is very poor because of the large statistical interaction among these components due to the fact that the carbon atoms all lie close to a circle (compare benzene: Cox, Cruickshank & Smith, 1958; Cruickshank, 1956). The reduced accuracy is shown by the larger e.s.d. for these components (Table 3) and by their large correlation coefficients computed but not listed in the Table.

The error in bond lengths due to the librational motion is uniformly less than 0·001 Å.

Molecular deformation and non-bonded repulsions

The most challenging problem posed by the molecular geometry is the inequality of the inner and outer C–C bond lengths. This is most unexpected since theoretical studies of the macrocyclic conjugated polyenes (Ooshika, 1957; Longuet-Higgins & Salem, 1959, 1960; Gouterman & Wagnière, 1960, 1962; Coulson & Dixon, 1962) have suggested only two likely structures for these compounds: one with all C–C bonds equal in length and a second with alternating long and short bonds. It is natural to assume that the structure is essentially of the first kind and that the inequality in bond lengths is caused by the same intramolecular repulsions that are evidently responsible for the nonplanarity of the molecule. A quantitative test of this assumption, however, shows it to be virtually untenable. If we suppose that, but for the non-bonded repulsions between adjacent internal C–H groups, all C–C bond lengths would be equal, that their stretching force constants are likewise equal, and that interaction and anharmonicity terms can be neglected, both for bond stretching and for angle bending, we have a simple mechanical system governed by a set of linear equations that express the requirement that the system be in equilibrium with respect to infinitesimal in-plane displacements of each of the atoms. These equations may be written:

$$k_1[\delta \cos (\theta+\psi)+\varepsilon]-k_2(\varphi+\psi) \sin (\theta+\psi)/(a+\delta)=0$$

$$k_1\delta \sin (\theta+\psi)+k_2(\varphi+\psi) \cos (\theta+\psi)/(a+\delta)=0$$

$$2k_1\delta \cos [(\theta+\varphi)/2]-2k_2(\varphi+\psi) \sin [(\theta+\varphi)/2]/(a+\delta)= -F\,.$$

In these equations (see Fig. 2) a is the unstrained C–C bond length, θ the unstrained C–C–C bond angle, allowing for geminal non-bonded interactions but not for the requirements of ring closure, k_1 and k_2 are the bond-stretching and angle-bending force constants, $a+\delta$ and $a+\varepsilon$ are the actual $C(\alpha)-C(\beta)$ and $C(\beta)-C(\gamma)$ bond lengths, $\theta+\varphi$ and $\theta+\psi$ are the actual C–C–C angles at $C(\alpha)$ and $C(\beta)$, respectively, and F is the radial force on atom $C(\alpha)$ due to non-bonded repulsions between the $C(\alpha)-H(\alpha)$ group and its neighbors inside the ring. Symmetry demands that this force be equal in magnitude to the net in-plane repulsion between each pair of adjacent internal C–H groups. Closure of the ring, which is nearly planar, requires that $\theta+2\psi-\varphi=120°$. The equations have the solution:

$$\delta=-F \cos (\theta+\psi)/k_1$$

$$\varepsilon=F/k_1$$

$$\varphi+\psi=F(a+\delta) \sin (\theta+\psi)/k_2\,.$$

Substituting the observed bond lengths and angles, we find

$$\varepsilon-\delta=r_O-r_I=0{\cdot}037 \text{ Å}=0{\cdot}444\ F/k_1$$

$$a=1{\cdot}336 \text{ Å}\,.$$

This last result implies an unstrained bond length equal to that in ethylene and must be rejected as absurd. Also, if we take $k_1=5{\cdot}15$ mdyne.Å^{-1}, given by Scherer & Overend's (1961) modified Urey–Bradley analysis of benzene, we obtain a repulsive force

$$F=42{\cdot}9\times 10^{-5} \text{ dyne}\,.$$

This is several times as large as the repulsion implied by any of the postulated non-bonded potential curves for C · · · C and H · · · H interactions (see *e.g.*, Coulson & Haigh, 1963).

The expression for $\varphi+\psi$ does not yield much useful information since, with θ unknown, there is no experi-

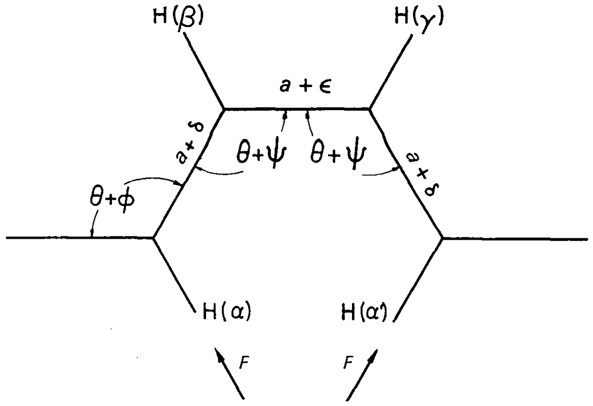

Fig. 2. Parameters for calculation of molecular in-plane deformation. Atoms 1, 2, 3, *etc.* have been relabelled α, β, γ, *etc.* in accordance with postulated $\bar{3}$ symmetry.

mental measure of φ or ψ. If we reasonably assume $\theta \geq 120°$ and adopt the Scherer–Overend value for $k_2 = 0{\cdot}663 \times 10^{-11}$ erg.rad^{-2}, we find

$$F \leq 11{\cdot}72 \times 10^{-5} \text{ dyne},$$

which is a far more reasonable result than the previous estimate. A value near the indicated limit would account for about 0·01 Å of the difference between r_I and r_O, leaving most of this difference still unexplained.

Although the attempt to explain the C–C bond lengths by non-bonded repulsions alone has been unrewarding, such repulsions undoubtedly exist and must be the principal cause of the molecular non-planarity. In attempting to account quantitatively for the out-of-plane deformation, we adopt a molecular configuration of $\bar{3}$ symmetry with average values of bond lengths, bond angles, and out-of-plane displacements. The repeat unit in this structure (Fig. 3) comprises one-sixth of the molecule. We assume force constants as estimated by Coulson & Senent (1955) for benzenoid aromatic hydrocarbons and generalized by Hirshfeld (1963) and suppose that the non-planarity arises mainly from the non-bonded repulsions F_c, between C(α) and C(α'), and F_h, between H(α) and H(α'), and similar forces between other pairs of atoms symmetrically related to these. The net out-of-plane repulsive forces acting on C(α) and H(α) are, respectively,

$$c_\alpha = 2F_c \sin \chi_c$$
$$h_\alpha = 2F_h \sin \chi_h$$

where χ_c is the inclination to the mean molecular plane of the line C(α) · · · C(α'), χ_h is the inclination of H(α) · · · H(α').

Rather than rely on the imprecisely determined hydrogen positions, we prefer to adopt standard C–H bond lengths (1·084 Å), assume equal C–C–H angles at each carbon atom, and take the out-of-plane hydrogen coordinates as adjustable parameters. These parameters, designated z_α, z_β, and z_γ, together with the repulsive forces F_c and F_h, are to be determined by a set of equations expressing the equilibrium conditions for out-of-plane displacements of the several atoms. Because of the suspicion (see above) that significant displacements may arise from intermolecular forces on C(3), C(6), and H(9), we introduce an unknown out-of-plane force $-c_\gamma$ acting (in a negative direction) on C(γ). [If it is true that the large out-of-plane coordinate of C(9) is caused by intermolecular repulsions at H(9), the fact that the molecule nevertheless displays $\bar{3}$ symmetry implies that these repulsions affect the carbon skeleton much as would a force, equal to that at C(3) and C(6), applied directly to C(9)]. There are now six parameters, including c_γ, and six equilibrium conditions, *i.e.* one for each of the six atoms in the repeat unit. The solution obtained is:

$$\begin{aligned}
z_\alpha &= 0{\cdot}137 \pm 0{\cdot}043 \text{ Å} \\
z_\beta &= -0{\cdot}037 \pm 0{\cdot}019 \\
z_\gamma &= -0{\cdot}053 \pm 0{\cdot}018 \\
c_\alpha &= (1{\cdot}22 \pm 0{\cdot}65) \times 10^{-5} \text{ dyne;} \\
h_\alpha &= (2{\cdot}13 \pm 0{\cdot}91) \times 10^{-5} \\
c_\gamma &= (-1{\cdot}24 \pm 0{\cdot}22) \times 10^{-5} \\
F_c &= (13{\cdot}7 \pm 7{\cdot}4) \times 10^{-5} \\
F_h &= (7{\cdot}3 \pm 0{\cdot}9) \times 10^{-5}
\end{aligned}$$

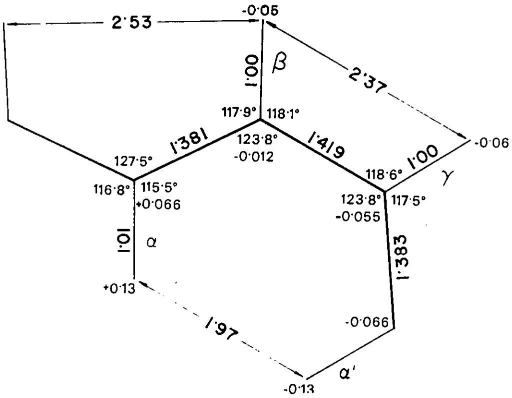

Fig. 3. Average interatomic distances and displacements from mean molecular plane, in Å, and bond angles, corresponding to $\bar{3}$ molecular symmetry.

The estimated standard deviations listed above include no explicit allowance for the uncertainty of the several assumptions underlying the calculation but reflect only the random errors in the experimental positions of the carbon atoms. These errors have, however, been conservatively estimated from the observed departure from $\bar{3}$ molecular symmetry in the experimental N coordinates. Thus we have treated any atomic displacements due to intermolecular forces, other than c_γ, as normally distributed independent variables analogous to experimental errors in the coordinates. The departures from $\bar{3}$ symmetry (see above) amount to 0·0098 Å r.m.s. for the nine carbon atoms in the asymmetric unit. But we have arrived at this figure after, in effect, fitting to the nine experimental out-of-plane coordinates five independent parameters: two independent direction cosines of the N axis and the average N coordinates of the three carbon atoms in the repeat unit (Fig. 3). With four remaining degrees of freedom, we have roughly estimated the standard deviations of the experimental N coordinates at $(\frac{9}{4})^{\frac{1}{2}} \times 0{\cdot}0098 = 0{\cdot}015$ Å, or 0·0085 Å for the coordinates of the three atoms in the repeat unit, each of which is the average of three experimental values. The hydrogen coordinates and the several derived forces listed above have all been calculated as explicit functions of these three carbon N coordinates so as to permit the direct evaluation of their standard deviations from those of the coordinates.

We note that the calculated hydrogen displacements agree remarkably well with the average experimental coordinates (Fig. 3). We should regard this agreement as excellent confirmation of the entire analysis, were the individual hydrogen coordinates (part I, Fig. 2) not so discordant among themselves as to render their averages patently meaningless.

The calculated value of F_c is clearly without experimental significance. The value of F_h, on the other hand, is both formally significant, much more so than its out-of-plane component h_α, and reasonable in magnitude. However, the value obtained for c_γ seems an order of magnitude too large for an intermolecular repulsion. Evidently we must either seek an alternative explanation for the absence of $\bar{3}m$ symmetry or else reject the Coulson–Senent force constants for this molecule. Speculation on this question is better deferred until the bond lengths have been satisfactorily explained.

Bond-length variation, other explanations

If non-bonded repulsions are inadequate to account for the observed bond-length variation, no other explanation we have tried has proved more successful. The possibility remains that the variation $\Delta r = r_O - r_I$ may be the result of several factors each contributing a small share of the total effect. Non-bonded repulsions surely constitute one of these factors. A second possible factor, related to this, may be associated with the large C–C–C bond angles. We have seen that these angles are increased by the intramolecular repulsions and are, therefore, strained. This means that the C–C σ bonding orbitals are bent, probably in the manner indicated in Fig. 4. The amount of bending is greatest for the inner bonds, *e.g.* C(α)–C(β), because of the large C–C–C angle (127·52°) at atom C(α); furthermore, the atomic orbitals forming this bond are inclined in opposite directions to the bond axis. By contrast, the atomic orbitals participating in the outer bond C(β)–C(γ) are bent less and in the same direction. If orbital bending of this sort can shorten the bonds in cyclopropane (Coulson & Moffitt, 1949), it may do so here too, though probably to a much lesser extent. This effect may, perhaps, cause something less than 0·01 Å of the difference Δr.

An additional possibility to be considered is that because of their different environments the inner and outer carbon atoms may differ slightly in electronegativity. This would cause a small charge μe (of unknown sign) on the outer atoms, $-2\mu e$ on the inner atoms, with the result that the outer bonds would be stretched an amount d while the inner bonds would contract by $2d$, where, with e in electrostatic units,

$$d = \mu^2 e^2 / k_1 a^2 \,.$$

For $|\mu| \sim 0{\cdot}1$, we should have a contribution to Δr of

$$3d \sim 0{\cdot}007 \text{ Å} \,.$$

If the bond-length variation is, in fact, made up of several small terms of this approximate magnitude, a proper calculation of the effect is bound to be difficult.

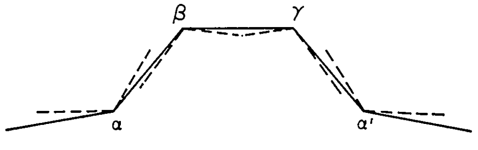

Fig. 4. Bending of bond orbitals due to strained valency angles. Broken lines show, schematically, axes of atomic orbitals forming C–C σ bonds.

Bond-alternation theory

Longuet-Higgins & Salem (1960) and Gouterman & Wagnière (1960) have interpreted the ultraviolet absorption spectrum of [18]annulene as implying an alternation in bond lengths around the ring. This interpretation is now seen to be invalid. Further, the discrepancy between the observed and calculated frequencies of the first ultraviolet absorption maximum, which had been ascribed to bond alternation, is not obviously resolved by the pattern of bond-length variation actually observed. If we assume unequal resonance integrals β_I and β_O for inner and outer bonds, respectively, simple Hückel theory gives the binding energies of the (doubly degenerate) highest occupied and lowest unoccupied π orbitals as

$$E_\pm = \pm 2[(2\beta_I^2 + \beta_O^2)/3]^{\frac{1}{2}} \cos (\omega + \pi/3)$$

where ω is the smallest positive root of the equation

$$\cos 3\omega = -\tfrac{1}{2}(\beta_I/\beta_O)^2[(2\beta_I^2 + \beta_O^2)/3\beta_O^2]^{-3/2} \,.$$

For $\beta_I = \beta_O = \beta$, the corresponding binding energies are

$$E_\pm{}^0 = \pm 0{\cdot}3473 \, \beta \,.$$

If β_I and β_O are allowed to vary in such a way that the average resonance integral $(2\beta_I + \beta_O)/3$ remains constant and equal to β, the binding energies slowly decrease in magnitude for small changes in β_I and β_O. On the basis of the expression adopted by Longuet-Higgins & Salem (1959) for the variation of resonance integral with bond length,

$$\beta = Be^{-r/a} \,,$$

with $a = 0{\cdot}3106$ Å, the observed bond-length difference $\Delta r = 0{\cdot}037$ Å corresponds to a ratio of resonance integrals

$$\beta_I / \beta_O = 1{\cdot}127 \,.$$

For this ratio, the binding energies given by the expression above are

$$E_\pm = \pm 0{\cdot}3443 \, \beta \,,$$

negligibly different from the result for $\beta_I = \beta_O$. It is clear, therefore, that the high frequency of the first absorption band, compared with theoretical predictions, must have a different explanation.

A similar conclusion applies to the nuclear magnetic resonance spectrum of [18]annulene, which has been cited in further support of bond alternation (Longuet-Higgins & Salem, 1960).

Gouterman & Wagnière (1962) have subsequently discarded the bond-alternation hypothesis, on the basis of their low-temperature ultraviolet spectral data for [18]annulene. They have not offered an alternative explanation for the position, or the intensity, of the ultraviolet absorption except to suggest that these effects, as well as the nuclear magnetic resonance spectrum of [18]annulene (Jackman, Sondheimer, Amiel, Ben-Efraim, Gaoni, Wolovsky & Bothner-By, 1962), may all be due to some unknown factor that reduces the mobility of the π electrons around the aromatic ring. If their suggestion is accepted, the observed variation in bond lengths may, perhaps, fill the role of the postulated unknown factor. Qualitatively, this is the behavior we should expect; the π electrons will tend to be localized in the six pairs of shorter, inner bonds as a result of the smaller resonance integral of the outer bonds, which acts as a slight barrier between neighboring inner-bond pairs. We have not attempted a quantitative estimate of this effect in view of the uncertainty as to the reason, or reasons, for the bond-length variation.

The problems just considered, as well as the inconclusive result of the calculation of the out-of-plane deformation, point to the need for further theoretical study of this most challenging molecule.

We are grateful to Professor Franz Sondheimer and Dr Reuven Wolovsky for their encouragement of this investigation. We also benefited from stimulating discussions with Professor C. A. Coulson and, by correspondence, with Mr C. W. Haigh. Mr Reuben Cohen prepared the diagrams.

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The Crystal Structure of the Red Potassium Molybdenum Bronze, $K_{0\cdot26}MoO_3$

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(*Received* 19 *November* 1964)

$K_{0\cdot26}MoO_3$ crystallizes in the monoclinic system, space group $C2/m$, with the unit-cell dimensions $a=14\cdot278$, $b=7\cdot723$, $c=6\cdot387$ Å, $\beta=92°\ 34'$. Its structure, determined by image-seeking and refined by three-dimensional differential Fourier syntheses and also by least squares, contains distorted Mo–O octahedra grouped by edge-sharing into units of six. These units share corners and form layers, with potassium ions occupying irregular eight-coordinated interlayer positions. Similarities to molybdenum oxides and oxyacids are discussed.

Introduction

The term *bronze* is used as a trivial name to describe a class of transition-metal oxide incorporating variable amounts of a third element, which is usually an alkali metal. Although the alkali tungsten bronzes were first prepared by Wöhler about 1824, it was not until recent years that the class was widened to include certain oxides of titanium, vanadium, niobium, platinum and palladium instead of tungsten. The crystal structures they adopt are not necessarily similar to one of the three known classes of tungsten bronze, and altogether