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CHEMICAL REACTION PATHS—VI

A PERICYCLIC RING CLOSURE

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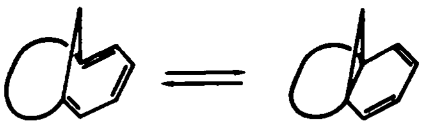
Abstract—Structural data from several crystal structure analyses of 1,6-methano annulenes and related molecules are used to map the reaction path for the pericyclic 1,6-ring-closure reaction. A possible structural expression of the attractive interaction between the reacting atoms can be detected.

According to orbital symmetry considerations[1] the disrotatory ring-closure/ring-opening reaction is a concerted process that should proceed with a low activation enthalpy. From NMR measurements[2,3] the actual barriers for several reactions of this type are around 7 kcal mole^{-1}.



The potential energy variation along the reaction path must then be relatively flat and its details should be sensitive to small changes in molecular structure and environment. Indeed, 1,6-distances observed in equilibrium (minimum energy) structures of several molecules of this type cover the range from 1·50 Å (covalently bonded) to 2·25 Å (essentially non-bonded).[4-10] We have therefore examined the available structural data for these molecules from the point of view that any observable correlation between the 1,6-distance and other structural parameters should map a path that lies close to the minimum energy path for the ring-closure reaction and throw light on the factors that determine such a path. This approach has already been used to obtain information about reaction paths for other types of reaction—S_N1[11], S_N2[12] and nucleophilic addition[13,14] to CO groups.

Structural data for the molecules **1-7** are summarized in Table 1. It is immediately obvious that as the 1,6-bond opens, the atoms 1 and 6 become less pyramidal and eventually pass through the plane of the three atoms to which they remain bonded. These changes are accompanied by changes in the ring angles and bond lengths. In particular, the bond length differences become less pronounced in the "open" annulenes. For several other systems the increment in an interatomic distance from the corresponding bond distance has been correlated with the pyramidality of one of the atoms, i.e. $\Delta d = f(\Delta)$ where Δ is the displacement of the atom concerned from the plane formed by its three bonded neighbours.[11-14] In the present case such a correlation between $d(1\text{–}6)$ and $\Delta(1)$ is obviously present, but here the two quantities are not necessarily independent; they may be related by the ring-closure conditions.

Consider a [10]annulene molecule with a 1,6-methano bridge (Fig. 1). If C_{2v} symmetry is assumed, then only eight non-zero Cartesian coordinates are required to fix the relative positions of the 11 skeletal C atoms. Alternatively, these positions may be fixed by choosing an appropriate set of eight internal coordinates. For example, we could choose the four non-equivalent bond distances: $d(1\text{–}2)$, $d(2\text{–}3)$, $d(3\text{–}4)$, $d(1\text{–}11)$, the two non-equivalent bond angles α and β, and the dihedral angles φ and Ψ (Fig. 1). The remaining distances and angles, and the out-of-plane displacement $\Delta(1)$, could then be found by rather tedious trigonometrical calculations. It is difficult to apprehend relationships between parameters in an eight-dimensional space but, fortunately, most of them stay nearly constant as $d(1\text{–}6)$ varies from 1·50 to 2·25 Å.

Table 1. Distances and angles in [10]-annulene and cycloheptatriene derivatives (compounds **1-3**: C_s-averaged, compounds **4-7**: C_{2v}-averaged)

Compound	$d(1\text{–}6)$	$\langle\Delta\rangle$	$\langle\alpha(C(3))\rangle$	$\langle\beta(C(2))\rangle$	$\langle\beta(C(2))\rangle^{a}_{corr}$	$\langle d(1\text{–}2)\rangle$	$\langle d(2\text{–}3)\rangle$	$\langle d(3\text{–}4)\rangle$	$\langle\varphi\rangle$	$\langle\psi\rangle$	Ref.
1	1·501 Å	0·32 Å[b]	122·2°	118·8°	119·3°	1·480 Å	1·351 Å	1·452 Å	108·1°	175·8	4
2	1·65	0·15	122·0	119·4	123·0	1·47	1·38	1·43	107·2	158·6	5
3	1·72	0·20	122·5	121·0	124·3	1·47	1·37	1·41	106·8	159·9	6
4	1·780	0·102	123·6	123·9	124·5	1·458	1·335	1·419	112·2	172·9	7
	1·836	0·083	123·6	123·8	124·1	1·453	1·348	1·431	112·4	172·6	
5	2·14	−0·02	125·7	122·0	126·2	1·44	1·39	1·41	110·2	157·4	8
6[c]	2·25	−0·08	128·8	122·5	124·0	1·44	1·38	1·37	111·5	166·6	9
7	2·257	−0·053	127·7	122·3	124·8	1·409	1·383	1·415	109·9	162·7	10

[a] Since the dihedral angle ψ between the planes 1256 and 2345 varies from one molecule to another, the values of $\langle\beta(C(2))\rangle$ been adjusted to correspond to a model with all six atoms planar.

[b] Calculated for three carbon substituents at 1·49 Å distance.

[c] Disordered crystal structure.

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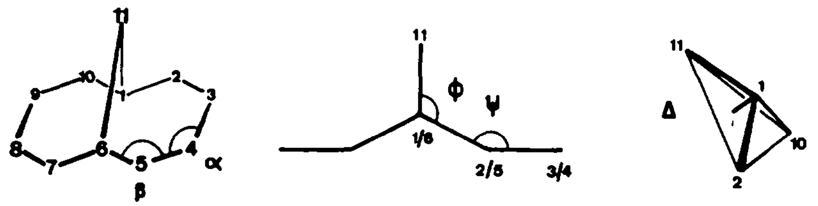


Fig. 1. 1,6-Methano [10]annulene numbering system and description of parameters α, β, φ, ψ and Δ.

Although the distances $d(1\text{–}2)$, $d(2\text{–}3)$ and $d(3\text{–}4)$ change systematically they do not vary by more than about 5% from 1·4 Å; similarly $d(1\text{–}11)$ varies by only a few percent from 1·5 Å and the dihedral angle φ stays in the range 107–112½°. The other dihedral angle ψ does vary, from about 155 to 175°, but the changes are unsystematic. The observed deviations from 180° in this angle (i.e. a non-zero value of the torsion angle around 2–3) help to lower the torsion angle around 1–2 and hence distribute the non-planarity of the π-system more evenly round the ring.[15] However, the actual value seems to depend more on the nature of the methano-substituents (and possibly on the crystal structure) than on the extent to which the ring-closure reaction has proceeded.

To simplify matters we discuss the reaction path in terms of an idealized molecular structure with $d(1\text{–}2) = d(2\text{–}3) = d(3\text{–}4) = 1{\cdot}40$ Å, $d(1\text{–}11) = 1{\cdot}50$ Å, $\varphi = 110°$, $\psi = 180°$ (values of β in Table 1 have been adjusted to this model by folding the plane 2345 to make the six atoms 123456 coplanar). With six internal coordinates now fixed, only two independent variables remain to be chosen, from Δ, $d(1\text{–}6)$, α and β, for example. We also require relationships to express the dependent variables in terms of the independent ones. One such relationship, expressing $d(1\text{–}6)$ in terms of α and β, is easily shown to be:

$$d(1\text{–}6) = 1{\cdot}4[1 - 4\sin(\beta/2)\sin(\alpha + \beta/2)]. \tag{1}$$

We now introduce the hypothesis that the ring-opening/ring-closure reaction path is the path along which the angle-strain energy is a minimum. This can be done by estimating the corresponding energy contribution, which is assumed to vary, approximately, as

$$S = k[(\alpha - \alpha_0)^2 + (\beta - \alpha_0)^2] \tag{2}$$

where the two angle-bending force constants and the two zero-strain angles are taken as equal. Since we are interested not in the actual value of the strain energy, but only in the α and β angles along the minimum energy path, we minimize (2) subject to the constraint (1) for various values of $d(1\text{–}6)$, the only remaining variable. The results are shown in Fig. 2 as three almost straight lines corresponding to three values of α_0 (120°, 122·5° and 125°). As an alternative we might consider how far a relationship of the type

$$d(1\text{–}6) = d(\text{C–C}) - c\,\log(\Delta/\Delta_{\max}) \tag{3}$$

could describe the reaction path. Relation (3) is defined only for positive Δ and it leads to infinite $d(1\text{–}6)$ when $\Delta = 0$. However, with reasonable values for $d(\text{C–C}) = 1{\cdot}50$ Å, $\Delta_{\max} \sim 0{\cdot}31$ Å (obtained from the closed molecule 1) and $c = 0{\cdot}71$ Å[16] it turns out that in the region 1·7–2·0 Å the path described by the logarithmic relation (3) is rather similar to the path derived from the condition of minimum strain energy (2) (Fig. 2).

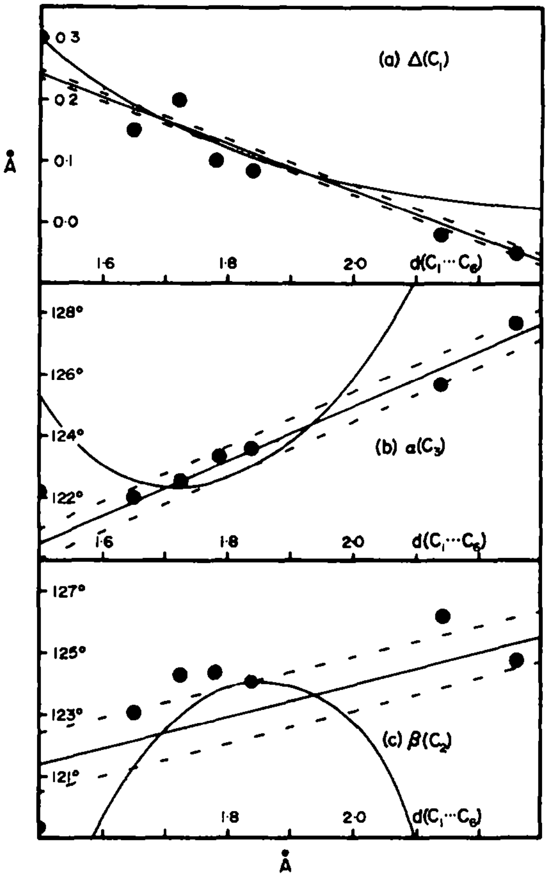


Fig. 2. Reaction path for ring-closure reaction. The curve shows the path determined by eqn (3). The straight lines show paths determined by the contribution of minimum angle strain at C(2) and C(3) for zero-strain angles α_0 of 125° (upper dashed line), 122·5° (full line) and 120° (lower dashed line). Experimental points from Table 1.

Comparison of the experimental data with the calculated curves shows that for $d(1\text{–}6) > 1{\cdot}7$ Å, the reaction path is well described by the angle-strain-minimization hypothesis. For the one case where $d(1\text{–}6) = 1{\cdot}5$ Å the experimental points are intermediate between the two curves.

On the whole, the observed structural correlation can be interpreted in terms of a reaction path controlled by angle strain at long $d(1\text{–}6)$ distances and influenced by a specific interaction between atoms 1 and 6 at short $d(1\text{–}6)$ distances. There are many other factors whose influence cannot be estimated so easily and we have chosen to ignore them in the present case. The disrotatory closure of 1,3,5-hexatriene to 1,3-cyclohexadiene has been investigated[17] using the MINDO/2 molecular orbital method. The transition state is calculated to be at $d(1\text{–}6) = 2{\cdot}06$ Å, $\Delta = 0{\cdot}26$ Å (calculated for three carbon substituents at

Table 2. Bond lengths and angles associated with the methano-bridge of various annulenes

Compound	α(C(1)–C(11)–C(6))	α(C(11)–C(1)–C(10))	α(C(11)–C(1)–C(2))	$\Sigma\gamma$	d(1–11)	Ref.
8	111·1°	120·5°	115·1°	346·7°	1·510(3) Å	19
		118·9	113·4	343·4	1·502(3)	
	106·5	115·3	117·9	339·7	1·511(3)	
9	105·8	119·1	117·3	342·2	1·520(5)	20
		121·6	113·7	341·1	1·502(5)	
	103·4	112·3	118·4	334·1	1·508(5)	
		121·1	117·2	341·7	1·505(5)	
10	103·6	119·4	115·5	338·5	1·487(4)	21
		120·5	116·0	340·1	1·493(4)	
11	102·4	119·2	117·9	339·5	1·479(4)	22
		119·3	118·0	339·7	1·482(4)	
12	102·0	119·9	117·1	339·0	1·489	23
		118·8	117·8	338·6	1·482	
7	99·6	116·3	114·3	320·2	1·477(9)	10
		117·0	116·8	333·4	1·477(9)	
13	94·8	118·5	118·9	332·2	1·477(5)	24
		115·8	117·4	328·0	1·509(5)	
5	92·4	115·5	116·9	324·8	1·470(10)	8
		117·9	117·1	327·4	1·490(10)	

1·40 Å distance), $\alpha = 120°$, $\beta = 122°$. The discrepancies between these values and the curves in Fig. 2 may be due to the open-chain character of 1,3,5-*cis*-hexatriene in contrast to the polycyclic character of the polyenes included in the structural correlations. Also, the values of certain types of structural parameter calculated by MINDO/2-methods are systematically different from the corresponding experimental values.[17]

Ermer[18] has recently pointed out that the lengthening of abnormally long C–C single bonds in saturated and unsaturated (non-conjugated) bicyclic molecules is roughly proportional to the net compression of the CCC-angles γ containing the bond in question, and has interpreted this in terms of 1,3-C ... C repulsive interactions. As far as methano-bridged annulenes (with d(1–6) > 2·1 Å) are concerned,[8,10,19–24] the correlation between bond lengths C(1)–C(11) and the corresponding bond angle sums ($\Sigma\gamma$) is just the opposite to that found by Ermer (Table 2, Fig. 3). Following Ermer's argument, we would have to conclude that in these molecules the 1,3-interaction between atom C(1) and C(6) is attractive over the entire range of C(1)–C(6) distances considered (1·5–2·48 Å).

The potential energy variation along the reaction path can be regarded as the resultant of a large number of attractive and repulsive terms, and the 1 ... 6 interaction is only one of these. Our conclusion that this interaction is attractive does not preclude the total potential energy from having a maximum somewhere along the reaction path. However, orbital symmetry considerations, in their simplest form, pertain only to the interaction, attractive or

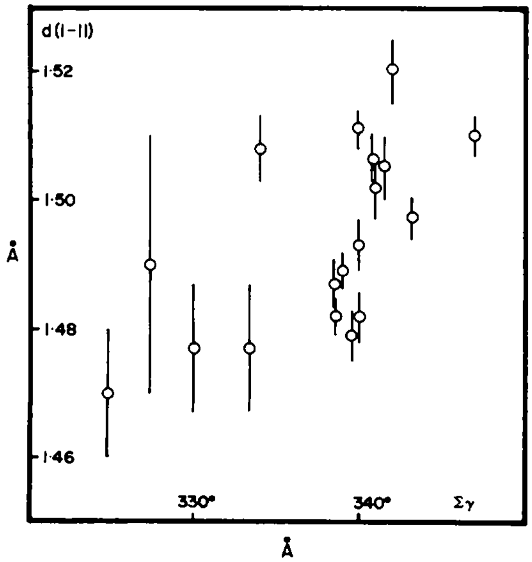
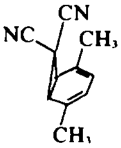
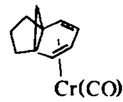
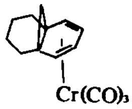
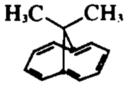


Fig. 3. Correlation plot of d(1–11) vs $\Sigma\gamma$ for molecules listed in Table 2. The vertical lines represent one standard deviation (estimates taken from the crystal structure analyses).









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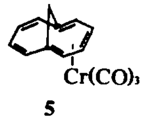

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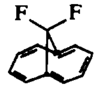

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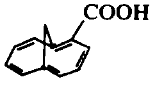

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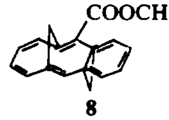

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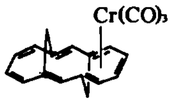

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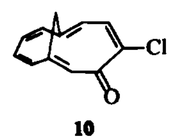

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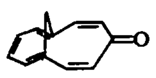

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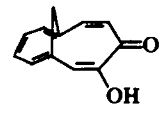

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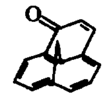

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repulsive, between the reacting atoms, and the correlation shown in Fig. 3 can therefore be regarded as a structural expression of an attractive interaction that follows immediately from the rules of orbital symmetry conservation.[1]

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