868. *The Structure of Molecules and Ions of the Type* $X_2A{\cdot}AX_2$, $X_2A{\cdot}AY_2$, *and* $YXA{\cdot}AXY$.

By P. J. WHEATLEY.

The structure of molecules and ions of the type $X_2A{\cdot}AX_2$, $X_2A{\cdot}AY_2$, and $YXA{\cdot}AXY$ has been examined in terms of the isoelectronic principle, and an attempt has been made to account for some of the observed regularities. Substances with 12, 24, or 36 electrons prove to be planar. Substances with 14, 26, or 38 electrons are non-planar. Those with 10, 22, or 34 electrons are usually planar, and probably always so in the gas phase, but in the solid strong lattice forces are sometimes sufficient to bring about a twisting of the two halves of the molecule. The observed structures of these simple molecules are used to indicate the general applicability of the isoelectronic principle to more complex molecules.

NUMEROUS substances of the type $X_2A{\cdot}AX_2$, $X_2A{\cdot}AY_2$, and $YXA{\cdot}AXY$ have been studied by physical methods, and their structures elucidated. Some of them have been the subjects of recent doubt or controversy.[1, 2] This paper correlates the known information in terms of the isoelectronic principle. Certain regularities in the shape and size of the molecules can be seen, and an attempt is made to account qualitatively for these observations, and to make some predictions. The fact that, as shown by Walsh,[3] there seem to be no exceptions to the isoelectronic principle when applied to simple molecules, suggests that prediction should not be too hazardous.

Simple Molecules.—In the Table a selection of molecules and ions is listed, together with the length of the central bond where known. The planarity of the molecule is indicated, and also the number of valency electrons. (If X or Y is polyatomic, the shape refers to the six central atoms, and the number of valency electrons is reckoned for these six atoms, counted in terms of the octet theory.) It will be seen that molecules with 10, 22, or 34 electrons, or with 12, 24, or 36 electrons are planar, but that molecules with 14, 26, or 38 electrons are non-planar. This correlation suggests that molecules such as $H_2N{\cdot}NO_2$ and B_2F_4 will be planar, whereas P_2H_4, N_2F_4, and Cl_2O_4, if they can be prepared and studied, will prove to be non-planar.

The central bond in molecules with 12, 24, or 36 electrons has the standard double-bond length. Molecules with 14, 26, or 38 electrons have a central bond length which is equal to, or a little longer than, a typical single bond. However, the molecules with 10, 22, or 34 electrons present a problem. It has long been puzzling that molecules such as oxalic acid should have the central atoms joined by what is apparently, from the length, a single bond. Nevertheless the information in the Table shows that this feature is common to many of the molecules with this number of valency electrons. Indeed, provided that both X and Y have unshared electron pairs, the preferrred π-orbitals seem to belong to each half of the molecule separately, with no conjugation occurring between the two halves. If, however, only one of X or Y had unshared pairs, as in $(CHO)_2$, $(Me{\cdot}CO)_2$, and $(MeC{:}NOH)_2$, then the central bond is shortened, and a π-orbital involving both halves of the molecule seems to be involved. There seem to be no exceptions to this rule [although $(COCl)_2$ might bear reinvestigation], and it suggests an interesting way of regarding oxalic acid and its isoelectronic analogues. In such molecules the unshared pairs seem to be affecting only the A–X and A–Y bonds and not the A–A bond. Thus, for a discussion of the length of the A–A bond, it seems legitimate to ignore the unshared electrons and concentrate on the σ-bond skeleton. It must be emphasised that this rather radical procedure can only be adopted if both X and Y have unshared electron pairs; it then justifies itself because the results which follow seem to agree with experiment.

In order to consider the σ-bond skeleton of these molecules, it is convenient to start with

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[1] Atoji, Lipscomb, and Wheatley, *J. Chem. Phys.*, 1955, **23**, 1176.

[2] Gray and Yoffe, *Quart. Rev.*, 1955, **9**, 385.

[3] Walsh, *J.*, 1953, 2260, 2266, 2288, 2296, 2301, 2306, 2318, 2321, 2325, 2330.

ethylene[4, 5] since it is probably the most extensively studied of these molecules. Ethylene has 12 valency electrons in orbitals which may be designated, in probable order of increasing energy, as a_{1g}, b_{1u}, a_{1g}, b_{2u}, b_{3g}, and b_{3u}.[5] The order of the five lowest orbitals is not particularly relevant to the present discussion, but it is imperative that the highest occupied orbital should be the b_{3u} or π orbital, and it is generally accepted that this is so. Above the b_{3u} or π orbital lies the b_{2g} or $\bar{\pi}$ orbital, which is not occupied in normal ethylene, but is occupied in hydrazine. A simple picture shows that the electrons in the π orbital have lowest energy when the two halves of the molecule lie in the same plane, whereas those in the $\bar{\pi}$ orbital have lowest energy when the two halves have their planes at right-angles. It is understandable, therefore,[5] that ethylene should be planar in the ground state, but possibly twisted in the first excited state, when one electron has been raised from the π to the $\bar{\pi}$ orbital, and that hydrazine should be twisted in the ground state. These remarks will be applicable to those analogues of ethylene which contain 24 and 36 electrons, and also to those analogues of hydrazine which contain 26 and 38.

Molecules and ions of the type $X_2A{\cdot}AX_2$, $X_2A{\cdot}AY_2$, *and* YXA·AXY *with the number of valency electrons and the* A–A *bond length* (Å).

Planar molecules.

Electrons	Compound	Bond length	Ref.	Electrons	Compound	Bond length	Ref.	Electrons	Compound	Bond length	Ref.
10	B_2H_4	—	—	34	$(CO{\cdot}NH_2)_2$	1·542	*e*	12	C_2H_4	1·34	*m, n*
				,,	$(CO_2Me)_2$	1·53	*f*	,,	,,	1·353	
22	$(CHO)_2$	1·47	*a*	,,	α-$(CO_2H)_2$	1·560	*g*				
				,,	β-$(CO_2H)_2$	1·57	*h*	24	$H_2N{\cdot}NO_2$	—	—
34	B_2F_4	—	—	,,	$(CO_2H)_2,2H_2O$	1·529	*i*	,,	$H_2C{:}CF_2$	1·311	*o*
,,	B_2Cl_4	1·75	1	,,	$(CO_2NH_4)_2,H_2O$ *	1·56	*j*	,,	$H_2C{:}CCl_2$	—	—
,,	N_2O_4	1·64	*b*	,,	$(COCl)_2$	1·50	*r*	,,	*cis*-$({:}CHMe)_2$	1·38	*p*
,,	$C_2O_4^{2-}$	1·54	*c*	,,	$(COMe)_2$	1·47	*a*	,,	*trans*-$({:}CHMe)_2$	1·40	*p*
,,	$(CS{\cdot}NH_2)_2$	1·544	*d*	,,	$(MeC{:}NOH)_2$	1·44	*l*				
	,,	1·534	*d*					36	C_2F_4	1·313	*o*
								,,	C_2Cl_4	1·30	*q*
								,,	$Me_2N{\cdot}NO_2$	1·30	*r*
								,,	,,	1·26	*s*

Non-planar molecules.

Electrons	Compound	Bond length	Ref.	Electrons	Compound	Bond length	Ref.	Electrons	Compound	Bond length	Ref.
14	N_2H_4	1·46	*t, u*	26	$Me_2N{\cdot}NH_2$	1·45	*v*	38	N_2F_4	—	—
,,	,,	1·47	,,	,,	$(NHMe)_2$	1·45	*v*	,,	Cl_2O_4	—	—
,,	P_2H_4	—	—					,,	$S_2O_4^{2-}$	2·389	*w*

* The oxalate ion in $(CO_2NH_4)_2,H_2O$ is non-planar.

There is experimental evidence for the shape of the molecule or ion only when a literature reference is cited.

[a] LuValle and Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 3520. [b] Broadley and Robertson, *Nature*, 1949, **164**, 915. [c] Jeffrey and Parry, *J. Amer. Chem. Soc.*, 1954, **76**, 5283. [d] Long, Markey, and Wheatley, *Acta Cryst.*, 1954, **7**, 140. [e] Ayerst and Duke, *ibid.*, p. 588. [f] Dougill and Jeffrey, *ibid.*, 1953, **6**, 831. [g] Cox, Dougill, and Jeffrey, *J.*, 1952, 4854. [h] Hendricks, *Z. Krist.*, 1935, **91**, 48. [i] Ahmed and Cruickshank, *Acta Cryst.*, 1953, **6**, 385. [j] Jeffrey and Parry, *J.*, 1952, 4864. [l] Merritt and Lanterman, *Acta Cryst.*, 1952, **5**, 811. [m] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 1223. [n] Gallaway and Barker, *J. Chem. Phys.*, 1942, **10**, 88. [o] Karle and Karle, *ibid.*, 1950, **18**. 963. [p] Brockway and Cross, *J. Amer. Chem. Soc.*, 1936, **58**, 2407. [q] Karle and Karle, *J. Chem. Phys.*, 1952, **20**, 63. [r] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46. [s] Costain and Cox, *Nature*, 1947, **160**, 826. [t] Collin and Lipscomb, *Acta Cryst.*, 1951, **4**, 10. [u] Giguere and Schomaker, *J. Amer. Chem. Soc.*, 1943, 2025. [v] Beamer, *ibid.*, 1948, **70**, 2979. [w] Dunitz, *ibid.*, 1956, **78**, 878.

In molecules with two electrons less than ethylene the two electrons dispensed with are those from the π orbital, and this leaves a single σ bond joining the two halves of the molecule. The same will be true of molecules containing 22 and 34 electrons, provided that the unshared pairs on X and Y can be ignored.

The planarity of ethylene is well understood, but the planarity of molecules with 10, 22, or 34 electrons is by no means obvious, unless only one of X and Y have unshared pairs,

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[4] Crawford, Lancaster, and Inskeep, *J. Chem. Phys.*, 1953, **21**, 678.
[5] Walsh, *J.*, 1953, 2325.

when conjugation between the two halves would tend to stabilise the planar form. It has been suggested that in oxalic acid electrostatic attraction between the hydroxyl and carbonyl oxygen atoms causes the planar form to be preferred,[6] but this seems implausible because the planarity persists when oxygen atoms are replaced by NH_2, Cl, and S. Of the orbitals that have been considered, b_{1u}, b_{3g}, and b_{2g} will tend to stabilise the twisted form of the molecule, whereas a_{1g}, a_{1g}, b_{2u}, and b_{3u} favour the planar configuration. Thus, of the six orbitals used in ethylene, four favour the planar configuration and two the twisted form, so that, if all orbitals are assigned the same weight, a planar C_2H_4 molecule is to be expected. Similarly, in the molecules with 10, 22, and 34 electrons, three of the orbitals favour a planar, and two the twisted, form so that the balance still favours planar structures. Unfortunately a similar argument applied to hydrazine and its analogues results in four orbitals favouring the planar and three the twisted form, yet the molecules are non-planar. It would be valuable to have sufficient information to construct correlation diagrams for molecules with 10, 22, or 34 electrons giving the energy of the orbitals as a function of the dihedral angle, because it does appear that an explanation for their planarity lies in the relative energy levels in the planar and twisted forms of the five orbitals occupied by the σ electrons.

If this statement is valid, some conclusions may be drawn about the spectra of these molecules, which may serve to test some of the assumptions made here. In passing from molecules with 12, 24, or 36 electrons to those with 10, 22, or 34 electrons, the two electrons which strongly favour the planar form have been eliminated. Thus molecules containing 10, 22, or 34 electrons will be " only just " planar. Relatively small forces might suffice to twist the molecule, and this is confirmed by the shape of the oxalate ion in ammonium oxalate hemihydrate, where the extensive hydrogen bonding seems able to twist the ion so that the dihedral angle is 28°. However, it appears from the Table that more than van der Waals forces are necessary to cause the distortion. Nevertheless, compared with that in ethylene, there will be only a small force constant opposing twisting in molecules with 10, 22, and 34 electrons leading, after allowance for mass factors, to a much lower value of the twisting frequency. Unfortunately this frequency is inactive in both the Raman and infra-red spectra of A_2X_4 molecules, but accurate values of the other frequencies are becoming available,[7, 8] and it is possible that the twisting frequencies will be deduced indirectly.

Even greater differences should be observable in the electronic spectra. In molecules with 12, 24, or 36 electrons an electron is first excited from the π to the $\bar{\pi}$ orbital, favouring a twisting of the molecule and a lowering of the twisting frequency. In molecules with 10, 22, or 34 electrons an electron will be excited to the π orbital, making the molecule much more firmly planar in the first excited state, and considerably increasing the twisting frequency.

More Complex Molecules.—Whether or not this interpretation is valid, there remains the large body of information in the Table which can be used to correlate and predict the structures of less symmetrical and more complex molecules. It will be noticed that we have been considering arithmetical series, with a difference of twelve; in less symmetrical molecules where, for instance, H with one valency electron might replace CH_3 with seven, the difference will be reduced to six, so that molecules with 12, 18, 24, 30, or 36 electrons will be planar. The number of applications that can be made is very large, and this discussion will be restricted mainly to some of those cases which have been confirmed experimentally.

Formamide has 18 electrons so that all the atoms should lie in one plane.[9] Oxamide has previously been regarded as (I). However, the system of atoms (II) is part of the oxamide molecule and has 24 electrons. Thus this part of the molecule must also be planar, and it follows that all the atoms in the oxamide molecule must lie in one plane. The same will be true of dithio-oxamide. Urea can be regarded as (III), which again has 24 electrons.[10]

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[6] Jeffrey and Parry, *Nature*, 1952, **169**, 1105.

[7] Ito and Bernstein, *Canad. J. Chem.*, 1956, **34**, 170.

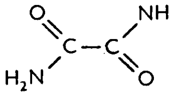
[8] Snyder, Hisatsune, and Crawford: Presented at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1956.

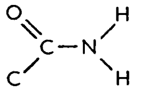
[9] Ladell and Post, *Acta Cryst.*, 1954, **7**, 559.

[10] Vaughan and Donohue, *Acta Cryst.*, 1952, **5**, 530.

Since each half of the molecule can be regarded separately, again the whole molecule must be planar. Guanidine and thiourea [11] can be similarly treated. The same argument can be applied to the amide grouping (II) in general, and there are several structures showing the planarity of this basic unit which plays such a large part in more complex molecules.[12] Similarly all the atoms except the methylene hydrogen atoms in ethylenethiourea [13] (IV) must be in one plane. The group of atoms shown in (V) is part of the benzene molecule, and again has 24 electrons. By taking the carbon atoms in pairs, it follows that the whole molecule is planar. Similarly dihydropyrazine (VI) will be planar. On the other hand, in 1 : 4-dithiin (VII) [14] a similar argument can only be applied to each half of the molecule. It follows that the molecule must have the boat form, but nothing can be said from these considerations about the planarity of the whole molecule. The same is true for the higher analogues such as thianthrene,[15] whereas naphthalene and anthracene must be totally planar.

Half of the *p*-dinitrobenzene molecule is shown in (VIII), and this has 34 electrons; the whole molecule should therefore be planar. However, this system is analogous to the oxalate ion, the C–N length being typically single with a value of 1·48 Å, and, as in ammonium oxalate, the lattice forces appear to be sufficient, even without the presence of hydrogen bonds, to cause a slight twisting so that the angle [16] between the planes of the nitro-group and the benzene ring is $9\frac{1}{2}°$.


(I)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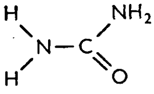
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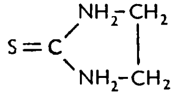
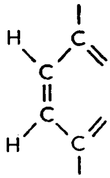
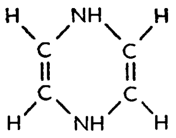
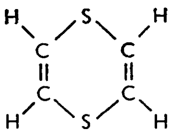
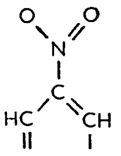
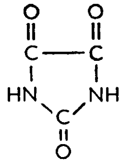

(IV)


(V)


(VI)


(VII)


(VIII)


(IX)

Finally parabanic acid (IX) is a molecule which illustrates well some of the points mentioned here.[17] The system of six atoms containing the two linked carbon atoms has 34 electrons, and the C–C bond has the typical single-bond value [18] of 1·541 Å. The other systems of six atoms have 30 electrons, so that the whole molecule is planar. It is also interesting to note that, whereas molecules of the type YXA•AXY adopt the *trans*-form, in parabanic acid the carboxyl groups must necessarily be *cis* to each other. The molecule is therefore under a form of constraint, which is insufficient, however, to remove the planarity.

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[11] Wyckoff, *Z. Krist.*, 1932, **81**, 386.
[12] Pauling and Corey, *Proc. Nat. Acad. Sci.*, 1951, **37**, 235.
[13] Wheatley, *Acta Cryst.*, 1953, **6**, 369.
[14] Howell, Curtis, and Lipscomb, *Acta Cryst.*, 1954, **7**, 498.
[15] Lynton and Cox, *J.*, 1956, in the press.
[16] Abrahams, *Acta Cryst.*, 1950, **3**, 194.
[17] Hughes, *Ann. Rev. Phys. Chem.*, 1955, **6**, 271.
[18] Davies and Blum, *Acta Cryst.*, 1955, **8**, 129.