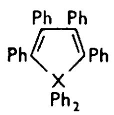
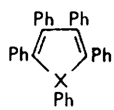
174. *The Electronic Structures of the Cyclopentadiene Analogues containing as Ring Member an Element of Group 5.*

By David A. Brown.

The electronic structures of cyclopentadiene analogues containing as ring member an atom of Group 5 are discussed in terms of simple molecular-orbital theory. It is suggested that the planar configuration has considerable conjugation energy by the use of the np_π-orbital of the hetero-atom. The inclusion of the nd_π-orbitals of the hetero-atom is considered unlikely to lead to much extra stabilization. The electronegativity parameters of these orbitals for elements of Group 5 are discussed and numerical estimates are obtained from spectroscopic work. The theoretical conclusions are compared with experimental evidence.

During the past two years, the isolation of new cyclopentadiene analogues containing one hetero-atom as ring member has been announced independently by two groups of workers.[1,2] The first group reported the existence of the basic structures (A) and (B). The second group reported heterocyclic compounds containing a Group 5 element, in

(A) 

 (B)

particular pentaphenylphosphole. This compound is quantitatively oxidized to the *p*-oxide in solution on exposure to air and undergoes normal Diels–Alder addition with maleic anhydride. It also forms π-complexes with iron pentacarbonyl, *e.g.*, $C_4Ph_5PFe(CO)_3$. In view of previous attempts [3] to describe the bonding of such π-complexes in terms of simple molecular-orbital theory and as a preliminary to discussing these new complexes in similar terms, we examined first the electronic structures of the above compounds from the point of view of simple molecular-orbital theory. We make the assumption that these compounds are planar and calculate their conjugation energies. A brief description of the theoretical methods and results are given first and then compared with experiment, where available.

We consider here only unsubstituted molecules in which the hetero-atom is a member of Group 5. It is necessary to consider the interaction of the $C(2p_\pi)$ atomic orbitals

[1] Leavitt, Manuel, and Johnson, *J. Amer. Chem. Soc.*, 1959, **81**, 3163.
[2] Braye and Hübel, *Chem. and Ind.*, 1959, 1250.
[3] D. A. Brown, *J. Inorg. Nuclear Chem.*, 1959, **10**, 39, 49.

situated on atoms 1—4 with both the np_π- and nd_π-orbitals (n = 3–5) of the hetero-atom X. The planar molecule falls into the C_{2v} symmetry group; the xy-plane is taken as the molecular plane and the yz-plane as the plane of two-fold symmetry. Under this symmetry classification the π-orbitals fall into the representation $3A_2 + 4B_2$ in which the antisymmetric A_2 group contains the nd_{xz}-orbital and the symmetric B_2 group contains the np_π- and nd_{yz}-orbital. Application of the usual variational method results in the secular determinant $|H_{ij} - S_{ij}E| = 0$, where H_{ij} and S_{ij} denote the resonance integral and overlap integral, respectively, between the orbitals ϕ_i and ϕ_j and H_{ii} denotes the Coulomb term of ϕ_i. Application of this method to the above molecule leads to one 3×3 determinant and one 4×4 determinant for the A_2 and the B_2 representation, respectively. A further simplification is achieved if overlap is neglected. For the hetero-atom X, it is necessary to take into account the difference in both the Coulomb terms of the np_π- and the nd_π-orbital and the resonance integral between these orbitals and the adjacent C($2p_\pi$) orbital from those of the normal C($2p_\pi$) orbital. This difference is related to the difference in the electronegativity between the hetero-atom X and a carbon atom. We assume that the above integrals are given by the expressions:

$$H(nd_\pi nd_\pi) = H_{cc} + \rho\beta_{cc};\ H(2p_\pi nd_\pi) = k\beta_{cc};$$

$$H(np_\pi np_\pi) = H_{cc} + m\beta_{cc};\ H(2p_\pi np_\pi) = n\beta_{cc},$$

where H_{cc} and β_{cc} denote the Coulomb term and the resonance integral, respectively, of the carbon $2p_\pi$-orbital and ρ, k, m, and n are parameters. We shall first consider the variation of the π-electron energy with these parameters and, secondly, attempt to assign reasonable values to them and thus to calculate the conjugation energies of the systems.

Neglect of d-*Orbitals*.—A direct solution of the problem involving the simultaneous variation of ρ, k, m, and n is too complicated since the B_2 group will give rise to a quartic involving all four parameters. Therefore, we shall first neglect the d-orbitals. In this case the A_2 group reduces to a simple quadratic identical with that obtained for the antisymmetric group in cyclopentadiene itself. The B_2 group gives rise to a cubic, $g(W)$, which is a function of the parameters m and n only; it takes the form

$$g(W) \equiv W^3 + W^2\beta(1 + m) - W\beta^2(1 - m + 2n^2) - (m + 2n^2) = 0,$$

where W is defined in the usual manner in the Hückel method. This equation was solved for the following range of values m = 0, ±0·5, ±1·0, ±1·5, ±2·0, and n = 0·2, 0·6, 1·0, 1·4, 1·8, 2·2, by means of an I.B.M. 602A computer. The total π-electron energy was then obtained for a given n and m value from the sum of the two lowest roots of the above equation together with the fixed lower root (−0·618β) of the A_2 quadratic. The variation of the total π-electron energy with n and m is shown in Fig. 1. A number of conclusions can be drawn. First, the π-electron energy increases with m, that is, with an increase in the Coulomb term of the hetero-atom (np_π) orbital. Secondly, the total π-electron energy increases with n, that is, with increasing values of the resonance integral between the np_π-orbital and the C($2p_\pi$) orbital. In our previous discussion [3] of the stability of complexes of the type $C_4H_4XFe(CO)_3$ it was shown that, in contrast to systems of the type C_4H_4CX, the molecule C_4H_4X possessed no suitable low-lying empty orbital which could be used for the back-donation required for the existence of stable complexes. The present work confirms the previous treatment in that for all values of m and n in the above range the lowest empty orbital lies above +0·640β; moreover, for a given m value it becomes increasingly antibonding with increasing value of n. It therefore appears that back-donation in such complexes is not likely to lead to much stabilization. It follows from the first of these conclusions that the total π-electron energy of our cyclopentadiene analogues will decrease with increasing size of the atom X in view of the general decrease in electronegativity on descent of a given Periodic Group. However, evaluation of the parameters m and n is needed for a quantitative discussion.

There has been much discussion as to the values of the parameters m and n to be employed in the simple Hückel treatment of conjugated systems containing a nitrogen atom, *e.g.*, pyridine and pyrrole. The original attempt by Wheland and Pauling [4] to introduce a type of self-consistency by spreading the m value over a number of carbon atoms adjacent to the hetero-atom has been shown [5] to be theoretically unsound. Indeed, many of the attempts to obtain a single value of m which through the L.C.A.O. M.O. method could satisfactorily predict a number of properties such as charge densities, spectral energies, has led to a range of m values (about 0·5—2·0). It is interesting that the more complete self-consistent field molecular-orbital theory gives values of the Coulomb terms which, if used for the calculation of m as defined above, result in excessively large m values. This is observed, for example, if one uses the relatively accurate Coulomb terms for nitrogen with core charges of both $+1$ and $+2$ calculated by Dewar and Paoloni [6] for melamine; this suggests that the correct value of m to be employed in the simple

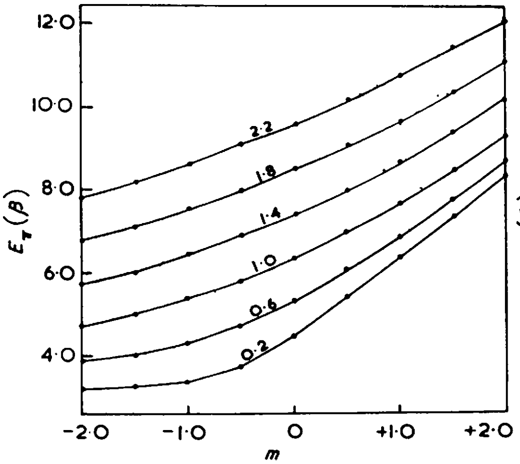


FIG. 1.

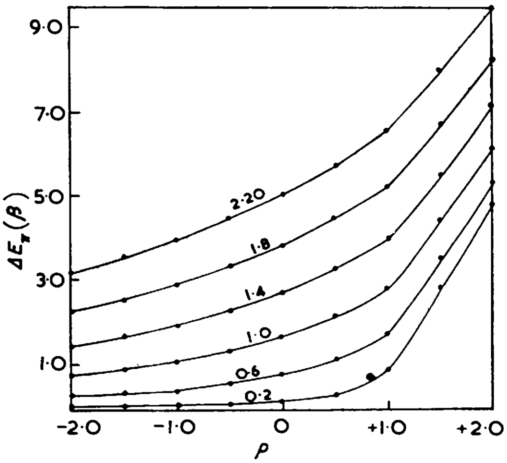


FIG. 2.

FIG. 1. Variation of E_π with the parameters m and n of $X(np_\pi)$. Values are n are stated on the curves.

FIG. 2. Variation of ΔE_π with the parameters ρ and k of $X(nd_\pi)$ ($m = 1$, $n = 1{\cdot}10$). Values of k are stated on the curves.

L.C.A.O. M.O. method is one which takes into account a number of opposing factors. Perhaps the best method of obtaining a satisfactory m value for the nitrogen core is by adjusting m to give the same charge distribution as that given by a more complete self-consistent field calculation, preferably by using the variable electronegativity self-consistent field (V.E.S.C.F.) method of R. D. Brown and his co-workers [7] in which the orbital exponent of an atomic orbital ϕ_i is regarded as a function of the electron density at that atom i. Treatment [8] of pyrrole by the latter method indicates an m value of 2·0. It is encouraging that the same value of m for nitrogen in quinoline gives a satisfactory explanation [9] of much of the observed chemistry of quinoline. However, no such methods are available for the other elements of Group 5, namely, phosphorus and arsenic; so we shall employ the general relationship $m_X = M(x_X - x_C)$, where x_X and x_C are the electronegativities of the hetero-atom X and carbon, and M is a proportionality constant. That

[4] Wheland and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2086.
[5] McWeeny, *Proc. Roy. Soc.*, 1956, *A*, **237**, 355.
[6] Dewar and Paoloni, *Trans. Faraday Soc.*, 1957, **53**, 261.
[7] R. D. Brown and Heffernan, *Trans. Faraday Soc.*, 1958, **54**, 757.
[8] R. D. Brown and Heffernan, *Austral. J. Chem.*, 1958, **12**, 319.
[9] R. D. Brown and Harcourt, *J.*, 1959, 3451.

a general relation should exist between the Coulomb term, H_{ii}, of an atom i and its electronegativity was pointed out first by Coulson and Longuet-Higgins [10] who suggested that the greater the electronegativity of atom i the greater the numerical value of H_{ii}. The general nature of the above relation has been discussed by Mulliken [11] and by Pritchard and Skinner.[12] It is not, however, generally permissible to assume that the proportionality constant M is unity: [13] it is preferable to determine M for a particular series. The electronegativity of an element in a particular valency state is then given by the relation [12] $x_X = (I + A)/6{\cdot}30$, where I and A are the ionization potential and electron affinity of atom X in the valency state under consideration. We shall determine I and A for the X^{2+} core of nitrogen, phosphorus, and arsenic, severally; the proportionality constant M will then be determined by comparing the above expression with the m value obtained from the V.E.S.C.F. method. The m values for phosphorus and arsenic will thus be obtained. To calculate I and A, we shall follow the method used by Dewar and Paoloni [6] to determine the energies of the transitions:

$$X^+\ (sp^3,\ V_3) \longrightarrow X^{2+}\ (sp^2,\ V_3) \qquad (I)$$

$$X^+\ (sp^3,\ V_3) \longrightarrow X\ (sp^4,\ V_3) \qquad (A)$$

Details of the cycles used to calculate the above quantities are given in the Appendix and we give only the results in Table 1. These values are, of course, only approximate but

TABLE 1.

The parameters m and n for elements of Group 5.

Element	I (ev)	A (ev)	x_X	m	n
C	—	—	1·90		
N	27·83	13·44	6·55	0·20	1·18
P	19·66	12·22	5·06	1·36	1·13
As	21·07	12·63	5·31	1·47	1·14

they serve as a basis for the calculation of the π-electron energies of the above systems. In order to determine the parameter n we assume that the resonance integral, H_{ij}, and the overlap integral, S_{ij}, between any two orbitals ϕ_i and ϕ_j are related by the expression $H_{ij} = \frac{1}{2}S_{ij}(H_{ii} + H_{jj})$. A general proportionality between the exchange integral and the overlap integral has been assumed by many authors [14] and is supported by a more recent theoretical analysis.[15] For the hetero-atom X bonded to an adjacent carbon atom we have

$$\beta_{CX} = \tfrac{1}{2}S_{CX}(H_{CC} + H_{XX});\ \beta_{CX} = \tfrac{1}{2}S_{CX}(2H_{CC} + m\beta_{CC});$$

but

$$\beta_{CC} = S_{CC}H_{CC};\ \beta_{CX} = \tfrac{1}{2}S_{CX}(2/S_{CC} + m)\beta_{CC}.$$

Calculation of the required $S(2p_\pi np_\pi)$ overlap integrals ($n = 2$—5) in terms of Slater functions [16] and with the assumption that the C–X distances are given by the sum of the covalent radii gave similar results for all the integrals:

$$S_{CC} = 0{\cdot}183;\ S_{CP} = 0{\cdot}191;\ S_{CAs} = 0{\cdot}190;\ S_{CSb} = 0{\cdot}172.$$

Hence

$$n \approx (1 + \tfrac{1}{2}mS_{CC}).$$

The values of n so calculated are given in Table 1. With the above assumptions, it is obvious that the Coulomb term of the hetero-atom i is more affected by a change in

[10] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.
[11] Mulliken, *J. Chim. phys.*, 1949, **46**, 497.
[12] Skinner and Pritchard, *Chem. Rev.*, 1955, **55**, 747.
[13] Laforgue, *J. Chim. phys.*, 1949, **46**, 568.
[14] Mulliken, *J. Chim phys.*, 1949, **46**, 500; Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173; Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.
[15] Rudenberg, *J. Chem. Phys.*, 1951, **19**, 1433.
[16] Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248; D. A. Brown, *ibid.*, 1958, **29**, 1086.

electronegativity than is the resonance integral. The total π-electron energy of these systems is then obtained from Fig. 1 by interpolation for the above values of m and n. The conjugation energy with respect to butadiene and the unconjugated hetero-atom may be calculated by subtracting from the total π-electron energy the sum of the π-electron energy of butadiene and the energy of the lone pair situated on the hetero-atom: $E_{\text{conj}} = E_\pi - (4{\cdot}472 + 2m)\beta_{\text{CC}}$. The π-electron energies and conjugation energies for the nitrogen, phosphorus, and arsenic compounds are then as follows:

$$\begin{array}{lll} X = N, & E_\pi = 9{\cdot}84\beta, & E_{\text{conj}} = 1{\cdot}37\beta. \\ X = P, & E_\pi = 8{\cdot}68\beta, & E_{\text{conj}} = 1{\cdot}49\beta. \\ X = As, & E_\pi = 8{\cdot}86\beta, & E_{\text{conj}} = 1{\cdot}45\beta. \end{array}$$

It follows that for all these compounds, both the total π-electron energy and the conjugation energy are considerable. The increase in conjugation energy with decreasing electronegativity is not surprising since more delocalization is then to be expected.

Inclusion of the d-*Orbitals of the Hetero-atom* X.—The variation of the π-electron energy with the parameters m and n having been established and reasonable values assigned to them, it is necessary to consider further the effect on E_π of the inclusion of the nd_{xz} and nd_{yz} orbitals of the hetero-atom X. In this case the antisymmetric A_2 group contains the nd_{xz}-orbital and gives rise to a cubic, whilst the symmetric B_2 group contains the nd_{yz}-orbital and so gives rise to a quartic. The cubic is simply a function of ρ and k and, with the values of m and n determined above, so too is the quartic. This equation takes the form:

$$A_2\colon f(W) \equiv W^3 - W^2\beta(1-\rho) - W\beta^2(\rho + 1 + 2\,k^2\sin^2\theta) + \beta^3[2\sin^2\theta\,(k^2-\rho)] = 0.$$

$$\begin{aligned} B_2\colon g'(W) \equiv\ & W^4 + W^3\beta(m+\rho+1) + W^2\beta^2[m\rho + m + \rho - 2n^2 - 2\cos^2\theta(k^2-1)] \\ & W\beta^3\{m\rho \dot{-} (m+\rho) - 2n^2(1+\rho) - 2\cos^2\theta\,[k^2\,(1+\mathrm{m})]\} \\ & - \beta^4[m\rho + 2n^2\rho + 2\cos^2\theta\,(mk^2)] = 0. \end{aligned}$$

2θ is the angle CXC. Two cases were considered for the parameters m and n, namely, $n = 1{\cdot}10$, $m = 1{\cdot}00$, and $n = 1{\cdot}10$, $m = 1{\cdot}50$, since this set is likely to cover most of the possibilities occurring with Group 5 elements. The parameters ρ and k were varied in the same manner as m and n. The cubic and the quartic were solved over this range by means of a Royal McBee LGP-30 computer, and total π-electron energy was calculated. The increase, ΔE_π in π-electron energy occurring on inclusion of the nd orbitals was plotted against k and ρ, for the two sets of m and n values, where $\Delta E_\pi = E_\pi(p + d) - E_\pi$. The values of E_π were obtained by accurate solution of $g(W)$ for the above values of m and n, together, of course, with the lowest root of the A_2 quadratic. The variation of ΔE_π with k and ρ is given in Fig. 2. It is evident that additional stabilization of the π-sytem through the inclusion of d-orbitals of the hetero-atom X increases with ρ and k. For small values of both ρ and k, however, the increase is very small indeed and under these conditions d-orbital participation results in little extra stabilization of the molecule. Unfortunately, it is extremely difficult to determine a reliable value of ρ. An attempt was made, however, in terms of the definition used above to determine m; that is, the electronegativity x_X for the nd-orbital was assessed from the relevant ionization potential (I_d) and the electron affinity (A_d) from the processes:

$$X^+\ (sp^2d, V_3) \longrightarrow X^{2+}(sp^2, V_3);\ X^+\ (sp^2d, V_3) \longrightarrow X(sp^2d^2, V_3).$$

Unfortunately, some of the spectroscopic results (see Appendix) required to calculate these quantities are lacking and the assumed values are not very reliable. So the ρ value for the $3d$-orbital of phosphorus (between $-0{\cdot}50$ and $-0{\cdot}70$) should be treated as approximate.

Certainly, it is reasonable that the 3*d*-orbital should have a Coulomb term smaller than the carbon $2p_\pi$-orbital. Fortunately, this ambiguity is not serious since it follows from application of the above formula for H_{ij} that for a considerable range of ρ values the parameter k is likely to be small.

From the above formula for H_{ij} we derive

$$k = \tfrac{1}{2}S(2p_\pi nd_\pi)(CX)[1/S(2p_\pi 2p_\pi)(CC) + \rho].$$

Employing the same procedure as above for the calculation of the required overlap integrals,[17] we find

$$S(2p_\pi 2p_\pi)(CC) \approx 0{\cdot}180;\ S(2p_\pi 3d_\pi)(CP) \approx 0{\cdot}060;$$

$$S(2p_\pi 4d_\pi)(CAs) \approx 0{\cdot}036;\ S(2p_\pi 5d_\pi)(CSb) \approx 0{\cdot}021,$$

and so for phosphorus, for example,

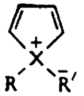
$$k \approx 0{\cdot}030(5{\cdot}556 + \rho).$$

It follows that even for a considerable range of the parameter ρ, *e.g.*, $-1{\cdot}0$ to $+1{\cdot}0$, the parameter k remains quite small (0·137—0·197). It is obvious then from Fig. 2 that for such small k values the extra stabilization energy, ΔE_π, is small and is less than 1 ev. These results suggest that in the phosphole participation of the 3*d*-orbitals of the phosphorus atom is not likely to increase the conjugation energy appreciably. This seems to support Zauli's recent contention [18] with regard to the use of the 3*d*-orbitals of the sulphur atom in thiophen. Unfortunately, even the scanty results for phosphorus are not available for arsenic or antimony, so that for them even approximate calculation of ρ values is impossible. However, from the calculated values of $S(2p_\pi 4d_\pi)$ and $S(2p_\pi 5d_\pi)$, it follows that the above argument is equally applicable to arsenic and antimony compounds. Of course, these conclusions are based primarily upon the small value of $S(2p_\pi nd_\pi)$ which arises from the disparity in the orbital exponents of the carbon $2p_\pi$- and hetero-atom nd_π-orbitals. It has been shown [19] that this disparity can be greatly decreased by contraction of the *d*-orbital in a potential field. Such a field could arise, *e.g.*, by attachment of strongly electronegative substituents, such as fluorine or chlorine, to the phosphorus atoms. It appears that this effect may be important in the case of the phosphonitrilic halides, $(PNX_2)_n$, where X is F or Cl and n is 3 or 4, for which the observed properties are reasonably consistent with $2p_\pi$–$3d_\pi$ interaction around the rings.[20] However, for the hetero-analogues of cyclopentadiene it seems implausible to assume that alkyl or aryl groups attached to the hetero-atom X can have such profound effects. We conclude, therefore, that these analogues containing hetero-atoms of Group 5 may possess reasonable conjugation energy by virtue simply of the use of their np_π-orbitals. The use of their *nd*-orbitals is not likely to lead to much extra stabilization.

Comparison with Experiment.—To date, few physical data have been reported for these compounds. The chemical behaviour of pentaphenylphosphole has been described briefly above. Perhaps the most noticeable feature is the ready formation [2] of the oxide $C_4Ph_5P^+–O^-$, in contrast with substituted pyrroles which tend to be oxidized by ring fission (2,4,5,*N*-tetraphenylpyrrole with potassium dichromate in acetic acid gives *cis*-dibenzoylstyrene [21]). For the pyrroles, failure to obtain nitrogenous products is ascribed to the instability of oxygenated cyclic systems in which the imine-hydrogen atom is substituted. In general, the inability of pyrrole to form complexes of the type $C_4H_5N^+–X^-$

[17] Jaffe, *J. Chem. Phys.*, 1953, **21**, 258; Leifer, Cotton, and Leto, *ibid.*, 1958, **28**, 364.
[18] Zauli, *J.*, 1960, 2210.
[19] Craig and Magnusson, *J.*, 1956, 4895.
[20] Craig, *J.*, 1959, 997.
[21] Spiro and Madonia, *Gazzetta*, 1955, **85**, 965.

is considered to be due to the loss of resonance energy upon the formation of the N^+–X^- bond.[22] However, this view requires a closer examination. Formation of a compound (C) probably converts the atom X from a planar valency state (sp^4,V_3), to a tetrahedral state ($s^{5/4}p^{15/4}$, V_3). The difference in energies of these states can be obtained very approximately by an interpolation method suggested by Moffitt;[23] it is found that the tetrahedral state lies several electron-volts below the planar and the difference is considerably greater for nitrogen than phosphorus. In other words, despite the fact that the quadrivalent state of X is more stable for nitrogen than phosphorus, it is in the latter field that one readily obtains a stable oxide. It may be contended, of course, that the extent of conjugation is very limited for the phosphorus compound and, consequently, there is no appreciable loss of conjugation energy on oxide formation. The above theoretical considerations, however, do not support this suggestion and an additional factor must be considered, namely, the relative strengths of the N–O and the P–O bonds. The P–O bond may be assumed to be similar to that in phosphorus oxychloride and in the phosphine oxides in which it is assigned[24] an energy of about 120 kcal. mole^{-1}. There are no comparable data for the analogous N–O bond which occurs in the amine oxides such as Me_3N^+–O^-. However, the N–O stretching force constant[25] in this molecule is 4—5 × 10^5 dynes cm.$^{-1}$, which may be compared with that of the N–O force constant in the nitrate ion[26] of 10·39 × 10^5 dynes cm.$^{-1}$ and here the N–O bond energy is about 90 kcal. mole^{-1}. In view of these values, it seems reasonable to assign a value of 30—50 kcal. mole^{-1} to the N–O bond energy in the above compounds. It follows that the greater value of the P–O bond energy may explain the relative ease of oxidation of phospholes than of pyrroles; consequently, the ease of oxidation is not necessarily an argument against conjugation in the parent phosphole. It is possible, of course, that for these systems the planar conjugated structure may have a ground-state energy similar to that of the non-planar structure in which the hetero-atom occupies a tetrahedral valency state. Further physical measurements of these compounds are awaited.



(C)

The above molecular-orbital treatment of the phosphole shows the absence of a vacant, low-lying π-orbital which would be required if back-donation is to occur from the iron tricarbonyl fragment to the π-system.[3] Since this effect is not facilitated, the phosphole may then act as a simple diene.

APPENDIX

Determination of Parameter m *for* np_π*-Orbitals*.—We require the ionization potential and electron affinity of the np_π-orbital, as given by the expressions:

$$I_{\text{p}}\colon\ X^+(sp^3, V_3) \longrightarrow X^{2+}(sp^2, V_3)$$
$$A_{\text{p}}\colon\ X^+(sp^3, V_3) \longrightarrow X(sp^4, V_4)$$

I_{p} may be obtained from the sequence:

$$X^+(s^2p^2,{}^3P_0) \longrightarrow X^{2+}(s^2p,{}^2P), \tag{1}$$
$$X^{2+}(s^2p,{}^2P) \longrightarrow X^{2+}(sp^2, V_3), \tag{2}$$
$$X^+(s^2p^2,{}^3P_0) \longrightarrow X^+(sp^3, V_3), \tag{3}$$

where (3) is taken as the mean of (4) and (5):

$$X^+(s^2p^2,{}^3P_0) \longrightarrow X^+(sp^3, V_2); \tag{4}$$
$$X^+(s^2p^2,{}^3P_0) \longrightarrow X^+(sp^3, V_4). \tag{5}$$

And $I_{\text{p}} = (1) + (2) - \tfrac{1}{2}[(4) + (5)]$.

[22] Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, New York, 1955, p. 136.
[23] Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **202**, 534.
[24] Charnley and Skinner, *J.*, 1953, 450.
[25] Goubeau and Fromme, *Z. anorg. Chem.*, 1949, **258**, 18.
[26] Schaefer and Bormuth, *Z. Phys.*, 1930, **62**, 508.

A_p may be obtained by averaging the processes:

$$X^+(sp^3, V_2) \longrightarrow X(sp^4, V_3), \qquad (6)$$

$$X^+(sp^3, V_4) \longrightarrow X(sp^4, V_3). \qquad (7)$$

And $A_p = \frac{1}{2}[(6) + (7)]$.

For nitrogen and phosphorus, the above quantities may be obtained from the extensive valency-state tables of Skinner and Pritchard.[27] For arsenic calculation of the quantities (6) and (7) required the additional processes (8) and (9):

$$X(s^2p^3, {}^4S) \longrightarrow X(sp^4, V_3), \qquad (8)$$

$$X(s^2p^3, {}^4S) \longrightarrow X^+(s^2p^2, {}^3P_0), \qquad (9)$$

whence $(6) = (9) + (4) - (8)$,

and $(7) = (6) + (4) - (5)$.

The above quantities were calculated by using Mulliken's valency-state formulæ [28] and those of the above authors. In general, the Slater parameters were adjusted to give the best representation of the observed spectral terms. We annex the results for arsenic.

Calculations for arsenic.

Transition	Energy (ev)	Parameters (cm.$^{-1}$)
(1)	20·20	—
(2)	9·58	$C = 104,623$; $G_1 = 21,814$; $G_2 = 2500$.
(4)	9·50	
(5)	7·93	$C = 94,086$; $G_1 = 8000$; $G_2 = 1815$.
(8)	7·47	$C = 71,887$; $G_1 = 2649$; $G_2 = 473$.
(9)	9·81	—

Determination of ρ *for* nd$_\pi$-*Orbitals*.—We require the quantities I_d and A_d:

$$I_d\colon X^+(sp^2d, V_3) \longrightarrow X^{2+}(sp^2, V_3)$$

$$A_p\colon X^+(sp^2d, V_3) \longrightarrow X(sp^2d^2, V_3)$$

The first quantity may be obtained from the sequence:

$$X^+(s^2p^2, {}^3P_0) \longrightarrow X^+(sp^3, V_3), \qquad (3)$$

$$X^+(sp^3, V_3) \longrightarrow X^{2+}(sp^2, V_3), \qquad (I_p)$$

$$X^+(s^2p^2, {}^3P_0) \longrightarrow X^+(sp^2d, {}^5P), \qquad (10)$$

$$X^+(sp^2d, {}^5P) \longrightarrow X^+(sp^2d, V_3). \qquad (11)$$

And $I_d = I_p + (3) - (10) - (11)$.

Similarly we have

$$X(s^2p^3, {}^4S) \longrightarrow X^+(s^2p^2, {}^3P_0), \qquad (9)$$

$$X^+(s^2p^2, {}^3P_0) \longrightarrow X^+(sp^2d, {}^5P), \qquad (10)$$

$$X^+(sp^2d, {}^5P) \longrightarrow X^+(sp^2d, V_3), \qquad (11)$$

$$X(s^2p^3, {}^4S) \longrightarrow X(sp^2d^2, V_3), \qquad (12)$$

and $A_d = (12) - (9) - (10) - (11)$.

The quantities I_p, (3), (9), and (10) have been calculated above or are available from Moore's tables.[29] However, the quantities (11) and (12) must be assessed. It is probable that the value of (11) is 2—3 ev, since (sp^2d, V_3) is a valency state lying above a state of maximum multiplicity. For phosphorus, Gillespie [30] suggested that the quantity (12) is 25—30 ev. With these very approximate estimates, it is found that the sum $(I_d + A_d)$ lies between 2 and 5 ev.

[27] Skinner and Pritchard, *Trans. Faraday Soc.*, 1953, **49**, 1254.
[28] Mulliken, *J. Chem. Phys.*, 1934, **2**, 782.
[29] Moore, " Atomic Energy Levels," N.B.S. Circular 467/U.S. Government Printing Office, Washington D.C., Vols. I—II.
[30] Gillespie, *J.*, 1952, 1002.

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