1005. *The Electronic Structures of Difluorocarbene and the Difluoroamino-radical*

By J. P. SIMONS

The results of simple molecular orbital calculations for CF_2 and NF_2 are related to the spectroscopic, thermodynamic, and chemical properties. It is suggested that the ultraviolet spectrum of CF_2 is due to the transition ${}^1B_1 \longleftarrow {}^1A_1$, rather than ${}^1B_2 \longleftarrow {}^1A_1$ as proposed originally. A suggested assignment for the electronic absorption spectrum of NF_2 is consistent with reported data. The results of the calculations are developed to provide an explanation for the high thermodynamic stability, and low chemical reactivity, of CF_2 and NF_2.

IN comparison with CH_2 and NH_2, the general chemical reactivity of CF_2 and NF_2 in their ground electronic states is very low. Their dimerisation proceeds relatively slowly, and they are thermodynamically stable, so that reactions involving them yield a relatively small nett gain in energy.[1-3] It has been suggested that the chemistry of CF_2 is closer to that of a two-electron deficient molecule than a biradical.[1]

Green and Linnett found that a simple molecular orbital calculation of the orbital energies and coefficients of NO_2 is a most successful aid in understanding some of its physical and chemical properties,[4] especially its dimerisation, ionisation, and electronic and e.m.r. spectra. In the discussion which follows, simple molecular orbital calculations of the electronic structures of CF_2 and NF_2 are shown to give results which account for their reported spectral, thermodynamic, and chemical properties.

Although the central bonds in perfluoroethylene and perfluorohydrazine are slightly

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[1] J. P. Simons and A. J. Yarwood, *Nature*, 1961, **192**, 943.

[2] F. Gozzo and C. R. Patrick, *Nature*, 1964, **202**, 80.

[3] J. W. Edwards and P. A. Small, *Nature*, 1964, **202**, 1329.

[4] M. Green and J. W. Linnett, *Trans. Faraday Soc.*, 1961, **57**, 1.

shorter than in ethylene and hydrazine, the energy required for dissociation at the central bond is much smaller. Thus, $D(F_2C{-}CF_2) \leqslant 70$ kcal./mole [2,3] compared with $D(H_2C{-}CH_2) \sim 160$ kcal./mole,[5] and $D(F_2N{-}NH_2) = 20$ kcal./mole [6] compared with $D(H_2N{-}NH_2) = 57$ kcal./mole.[7] In order to explain these observations in C_2F_4, it has been proposed that during the dimerisation of CF_2 in its ground electronic state, $^1A_1$, the system passes through a transition state in which the carbenes are excited into a triplet, $^3B_1$, valence state.[8] The theory is extended to include the other halgenocarbenes, and further developed to include the difluoroamino-radical.

Calculations.—The approximate calculation of the electronic energy levels in a triatomic molecule of C_{2v} symmetry has been described.[4] Group molecular orbitals were composed through linear combination of atomic orbitals of appropriate symmetry, using the three $2p$ orbitals on the F atoms, and the $2s$ and three $2p$ orbitals on the central atom (hereafter designated X). The $1s$ and $2s_F$ orbitals were not included.

The energies of the molecular orbitals were calculated by the Variation Method. For simplicity, it was assumed that all overlap integrals, and resonance integrals between non-adjacent atoms, were zero; thus, the numerical data required in the solution of the determinants included: (i) the difference between the Coulomb integrals for the $2s$ and $2p$ orbitals on the central atom $[\alpha(X_s) - \alpha(X_p)]$, and between the Coulomb integrals for the $2p$ orbitals on the central and F atoms $[\alpha(X_p) - \alpha(F_p)]$; (ii) the resonance integrals for the C–F and N–F bonds; these are related to σ- and π-overlap of the $2p$ orbitals, $\beta(p\sigma)$ and $\beta(p\pi)$, and to σ-overlap of the $2s$ orbital on the central atom and a $2p$ orbital on the F atom, $\beta(sp\sigma)$; (iii) the C–F and N–F bond lengths and bond angles.

Numerical Data.—(a) *Geometries.* The infrared spectrum of CF_2, trapped in a rigid matrix of argon or nitrogen at 4°K, has been recorded.[9] The vibration frequencies measured have permitted an estimate of the bond angle of $\sim 108°$; the C–F bond length is estimated to be $\sim 1{\cdot}32$ Å, as in C_2F_4 (where $\angle$FCF is 114°).

In NF_2 a bond angle of 104° has been determined,[10] assuming an N–F bond length of 1·37 Å as in the ground state of NH_3.

On the basis of Walsh's " rules," [11] the estimated bond angle in CF_2 seems a little low, and an angle of 110° has been chosen for the calculations. (In fact, the energies caclulated were relatively insensitive to small changes in the bond angle.)

(b) *Coulomb integrals.* Green and Linnett [4] estimated $\alpha(N_p) - \alpha(O_p)$ to be 1·5 ev, and noted that the difference in Coulomb integrals in C, N, and O is closely proportional to the difference in electronegativities of the atoms. On Pauling's scale, the relevant electronegativities are C = 2·5, N = 3·0, O = 3·5, and F = 4·0, and on this basis $\alpha(C_p) - \alpha(F_p) \sim 4{\cdot}5$ ev and $\alpha(N_p) - \alpha(F_p) \sim 3{\cdot}0$ ev. The energy differences $\alpha(C_p) - \alpha(C_s)$ and $\alpha(N_p) - \alpha(N_s)$ were estimated at ~ 8 and ~ 10 ev, respectively, on the basis of spectral data for C and N atoms.

(c) *Resonance integrals.* (i) *Difluorocarbene.* The Lennard-Jones method of estimating resonance integrals from spectral data was used successfully by Green and Linnett,[4] and the same method has been employed here. Andrews and Barrow [12] proposed that the upper state of CF, populated in the transition $B \longleftarrow X(^2\Pi)$, is probably the first excited $^2\Pi$ level; this transition promotes an electron from a π-bonding orbital into a π-antibonding orbital. A simple molecular orbital treatment gives the expression

$$\Delta E = \{[\alpha(C_p) - \alpha(F_p)]^2 + [2\beta(p\pi)]^2\}^{\frac{1}{2}}$$

[5] H. M. Frey, *Progr. Reaction Kinetics*, 1964, **2**, 131.

[6] J. T. Herron and V. H. Dibeler, *J. Chem. Phys.*, 1961, **35**, 747.

[7] J. A. Kerr, R. C. Sekhar, and A. F. Trotman-Dickenson, *J.*, 1963, 3217.

[8] J. P. Simons, *Nature*, 1965, **205**, 1308.

[9] D. E. Milligan, D. E. Mann, M. E. Jacox, and R. A. Mitsch, *J. Chem. Phys.*, 1964, **41**, 1199.

[10] M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, and D. E. Mann, *J. Chem. Phys.*, 1961, **35**, 1129.

[11] A. D. Walsh, *J.*, 1953, 2266.

[12] E. B. Andrews and R. F. Barrow, *Proc. Phys. Soc.*, 1951, **64**, 481.

for the difference in π-orbital energies. Taking $\Delta E = 6{\cdot}1$ ev,[12] $\beta(p\pi)$ in CF is 2·05 ev. In CF_2, the integral will be smaller because of the increased C–F bond length, and, on the assumption that resonance integrals are proportional to the corresponding overlap integrals, $\beta(p\pi)$ in CF_2 is estimated as ~1·9 ev. The remaining resonance integrals can be estimated if the same assumption is made, and are taken as $\beta(p\sigma)$ ~3·7 ev and $\beta(sp\sigma)$ ~4·9 ev. (The required overlap integrals were taken from the data of Mulliken *et al.*[13]).

(ii) *Difluoroamino-radical.* Unfortunately, spectral data relating to the NF radical are not available. In order to estimate the resonance integrals for the N–F bonds in NF_2, it was again assumed that these are proportional to the relevant overlap integrals, and that the proportionality constant is identical with that for CF_2, or for NO_2; (it may be noted that, in all three molecules, it is the same pair of atomic orbitals which is involved). The values estimated in this way, either from the data for CF_2 indicated above, or from the data[4] for NO_2, are shown in Table 1. The close agreement between the two sets of values lends additional support to the assumptions made.

TABLE 1

Resonance integrals for NF_2, in ev

	Calc. from CF_2	Calc. from NO_2
$\beta(p\pi)$	1·30	1·31
$\beta(p\sigma)$	3·28	3·16
$\beta(sp\sigma)$	2·73	2·67

The values chosen for the calculation were $\beta(p\pi) = 1{\cdot}3$ ev, $\beta(p\sigma) = 3{\cdot}2$ ev, and $\beta(sp\sigma) = 2{\cdot}7$ ev. To allow for the different orientations of the $2p_F$ and $2p_X$ orbitals in the molecular plane, it was necessary to multiply $\beta(p\pi)$ and $\beta(p\sigma)$ either by sin θ or cos θ as appropriate (where 2θ is the bond angle).

RESULTS

The energies which were calculated are represented in Figures 1 and 2, together with those[4] for NO_2. In each case the zero on the energy scale corresponds to the Coulomb integral, $\alpha(X_p)$, of the central atom. Since NO_2 and NF_2 have the same central atom, their orbital energies are indicated on the same diagram, and may easily be compared.

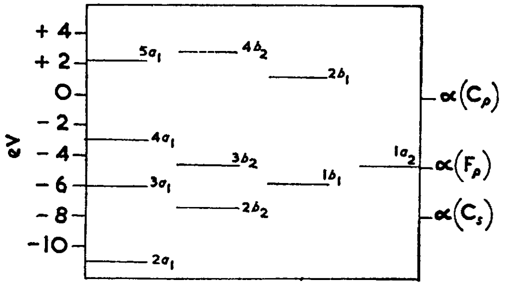

FIGURE 1. Orbital energies of CF_2

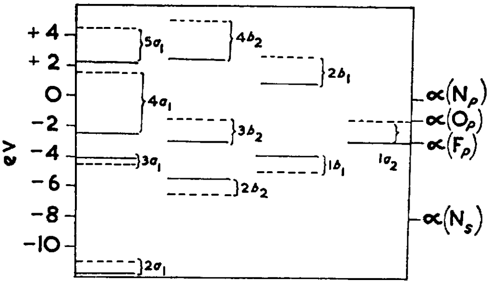

FIGURE 2. Orbital energies of NF_2 (——) and NO_2 (— — —)

For each molecule, the general order of the orbital energies is the same. CF_2 has eighteen electrons, and in its ground electronic state the outermost occupied orbital will be $4a_1$; it will be doubly filled, and the ground state will be $^1A_1$, as is well known. The nineteenth electron in NF_2 will lie in the $2b_1$ orbital. The relative spacing of the orbitals in NF_2 and CF_2 is, however, very different from that in NO_2. In particular, the outermost electrons in CF_2 and NF_2 are much more tightly bound. For example, the difference between the $3a_1$ and $4a_1$ orbital energies is only 3·1 and 1·6 ev in CF_2 and NF_2, compared

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[13] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

with 6·0 ev in NO_2; on the other hand, for the $4a_1$ and $5a_1$ orbitals, the separations are 5·2 and 4·7 ev in CF_2 and NH_2, compared with only 3·0 ev in NO_2. The increase in the binding energy of the $4a_1$ orbital must be due to the strong inductive effect of the F atoms; some of the consequences of this are discussed later.

The atomic orbital coefficients in the $1b_1$ and $2b_1$ molecular orbitals have been determined, and are given in Table 2; for comparison, the coefficients for NO_2 are also given. The two orbitals represent the π-overlap of $2p_F$ and $2p_X$ atomic orbitals perpendicular to the molecular plane, either in-phase ($1b_1$) or out-of-phase ($2b_1$). It is evident at once that there is appreciable partial double-bond formation, both in CF_2 and NF_2. (The agreement between coefficients in the two cases is fortuitous, but it does underline the parallel behaviour of the two species.) This will be more pronounced in CF_2, where the antibonding $2b_1$ orbital is empty in the ground state. Some contribution from π-bonding has previously been suggested in NF_2 [14] and in CBr_2.[15]

TABLE 2

Orbital coefficients (c_X, c_F) of the b_1 molecular orbitals

	CF_2	NF_2	NO_2
$1b_1$	0·425, 0·640	0·430, 0·640	0·628, 0·549
$2b_1$	0·910, −0·300	0·900, −0·300	0·777, −0·444

DISCUSSION

Spectroscopy.—(a) *Difluorocarbene.* The only electronic transition that has been reported in CF_2 has its origin at ~2650 Å; [16] this corresponds to an energy of 4·66 ev. The lower state involved in the transition is certainly the ground singlet, ${}^1A_1$. The rotational fine structure has been interpreted as indicating an electronic transition polarised parallel to the F–F line,[17] requiring the upper state to have the symmetry B_2; the spectrum has been assigned to the transition ${}^1B_2 \longleftarrow {}^1A_1$.

There is a ${}^1B_2$ state which has the configuration $\ldots(3b_2)^1(4a_1)^2(5a_1)^1$. The calculations presented would place this at ~6·8 ev above the ground state (or even higher if this energy represents the centre of gravity of a ${}^1B_2$ and a ${}^3B_2$ state). In addition, as Walsh has remarked,[11] this transition should not lead to the very marked increase in bond angle that is indicated by the long progression in the bending frequency ν_2'. However, it should lead to a very large change in the C–F bond length, since the $5a_1$ orbital is strongly σ_{C-F} antibonding; neither of the two stretching frequencies can be observed in absorption.[16,18] The present calculations, and Walsh's arguments, exclude this ${}^1B_2$ state as the upper level. Walsh was led to suggest that the upper state might instead have the electronic configuration $\ldots(4a_1)^1(4b_2)^1, {}^1B_2$. However, the energy calculated for this level is ~5·8 ev (or possibly higher), and is again far higher than the observed energy associated with the ultraviolet spectrum. In either case, several transitions at longer wavelengths would be anticipated and none have yet been found, even under conditions where the known absorption is very intense. Finally, any alternative B_2 states would lie at still higher energies.

The lowest excited singlet state of CF_2 will have B_1 symmetry and the electronic configuration $\ldots(4a_1)^1(2b_1)^1$. It is calculated to lie at an energy $\geqslant 4·2$ ev above the ground state; this is much closer to the observed transition energy than either of the two lowest ${}^1B_2$ levels. The transition should cause a marked increase in bond angle, and the placing of an electron in the $2b_1$ π-antibonding orbital should increase the C–F bond length. However, the increased bond angle will increase the C_{2s} character of the σ_{C-F} bonds, which will

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[14] J. Kaufman, *J. Chem. Phys.*, 1962, **37**, 759.

[15] P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, 1956, **78**, 5430.

[16] D. E. Mann and B. A. Thrush, *J. Chem. Phys.*, 1960, **33**, 1732.

[17] P. Venkateswarlu, *Phys. Rev.*, 1950, **77**, 676.

[18] B. A. Thrush and J. J. Zwolenik, *Trans. Faraday Soc.*, 1963, **59**, 582.

tend to offset any increase in $r_{\mathrm{O-F}}$. Little excitation of the upper-state stretching frequencies would be expected, as is observed experimentally.

On the basis of these arguments, one is led to question the interpretation of the rotational structure in the band spectrum of CF_2, in terms of a parallel transition, since the transition ${}^1B_1 \longleftarrow {}^1A_1$ will give rise to perpendicular bands. The parallel nature of the transition does not appear, in fact, to be completely established since the rotational structure reported by Venkateswarlu can be equally well interpreted in terms of a perpendicular transition,[19] and it is understood that attempts are being made [19] to check the polarisation by obtaining the bands under high resolution in absorption. It is proposed, therefore, that the electronic absorption of CF_2 be assigned to the transition

$$\ldots(4a_1)^1(2b_1)^1,{}^1B_1 \longleftarrow \ldots(4a_1)^2,{}^1A_1$$

and not to a ${}^1B_2$ state as originally proposed.[17]

In contrast to CF_2, the lowest-energy electronic transitions which have been observed in other isoelectronic triatomic molecules all lie at longer wavelengths. In SO_2, for example, the transition ${}^1B_1 \longleftarrow {}^1A_1$ probably lies in the near-ultraviolet,[20] and in O_3 the first electronic transition lies in the red.[21] In CH_2, the analogous transition also lies in the red.[22] The pronounced blue shift in CF_2 is readily explained by the large increase in the energy with which the outermost electrons (in the $4a_1$ orbital) are bound.

(b) *Difluoroamino-radical.* As with CF_2, at present only one electronic transition of NF_2 in known. The absorption is centred around 2600 Å,[23] with a long-wavelength limit at ~2780 Å. Although the rotational structure is destroyed by predissociation, vibrational structure can still be resolved. The spacing of the vibrational bands is ~380 cm.$^{-1}$, and has been assigned to the bending frequency of the upper state, ν_2'.[23] It has been suggested [24] that the spectrum be assigned to one or other of the two transitions,

$$\begin{array}{lll} \ldots(4a_1)^2(2b_1)^0(5a_1)^1,{}^2A_1 \longleftarrow & & (1) \\ & \ldots(4a_1)^2(2b_1)^1,{}^2B_1 & \\ \ldots(4a_1)^1(2b_1)^2,{}^2A_1 \longleftarrow & & (2) \end{array}$$

The energies calculated for these are ~1·3 and ~3·4 ev; since the long-wavelength limit of the absorption spectrum lies at ~4·5 ev, transition (1) can definitely be excluded.

A third possibility which might be considered, is the transition

$$\ldots(1a_2)^1(3b_2)^2(4a_1)^2(2b_1)^2,{}^2A_2 \longleftarrow \ldots(4a_1)^2(2b_1)^1,{}^2B_1 \qquad (3)$$

calculated to require ~3·9 ev. Walsh has assigned the near-ultraviolet absorption of the isoelectronic molecule ClO_2 to this transition.[11, 25] However, transition (3) would only lead to a small decrease in bond angle, and it seems unlikely that the absorption can be assigned to this.

An alternative transition, which would lead to a large increase in bond angle, is

$$\ldots.(4a_1)^1(2b_1)^1(5a_1)^1,{}^2B_1 \longleftarrow \ldots(4a_1)^2(2b_1)^1,{}^2B_1 \qquad (4)$$

which is calculated to require ~4·7 ev (or higher, if states of different multiplicity are taken into consideration). However, the transition would lead to a very large increase in the N–F bond length, and no sign of the stretching frequencies ν_1' and ν_3' can be detected in the absorption spectrum.

It is probable, therefore, that the observed transition is (2), with the excited ${}^2B_1$ level in (4) responsible for the predissociation. The corresponding transitions in NH_2 and NO_2 lie in the red, since the outermost a_1 electrons are much less tightly bound.

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[19] A. D. Walsh, personal communication.

[20] N. Metropolis and H. Beutler, *Phys. Rev.*, 1940, **58**, 1078.

[21] O. R. Wulf, *Proc. Nat. Acad. Sci.*, 1930, **16**, 507.

[22] G. Herzberg, *Proc. Roy. Soc.*, 1961, *A*, **262**, 291.

[23] F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.

[24] P. L. Goodfriend and H. P. Woods, *J. Mol. Spectroscopy*, 1964, **13**, 63.

[25] C. M. Humphries, A. D. Walsh, and P. A. Warsop, *Discuss. Faraday Soc.*, 1963, **35**, 148.

It is just possible that the dark blue colour, observed when the equilibrium mixture $N_2F_4 \rightleftharpoons 2NF_2$ is rapidly frozen from the gas at 100°c,[23] could be due to transition (1) of NF_2. The absence of any colour in the gas could be explained if there were an appreciable blue shift in the transition on passing to the solid phase.

Bond Strengths in NF_2 *and* CF_2.—The results presented indicate considerable π-bonding in CF_2, and to a lesser extent in NF_2. The C–F and N–F bond strengths may be compared with those in the CF_3 radical, and in NF_3, where, as Kaufman has argued,[14] little contribution from π-bonding is to be expected. They can be estimated from the following data (all expressed in kcal./mole): $\bar{D}$(C–F) in $CF_4 = 116$; [26] $D(F_3C\text{–}F) = 123$; [27] $D(FC\text{–}F) \leqslant 120$; [18] $D(C\text{–}F) \leqslant 132$; [18] whence $D(F_2C\text{–}F) \geqslant 89$. $\bar{D}$(N–F) in $NF_3 = 65$; [28] $\bar{D}$(N–F) in $NF_2 = 70$; [29] whence $D(F_2N\text{–}F) \sim 55$. Thus, the C–F dissociation energy in CF_2 exceeds that in CF_3 by ~31 kcal./mole, and for NF_2 and NF_3 the difference in N–F bond strengths is ~15 kcal./mole. (It may be remarked that the molecular orbital calculation indicates about twice as much π-bonding in CF_2 as in NF_2).

Chemistry.—(a) *Dimerisation and dissociation*. The apparent conflict between the low dissociation energy and the short length of the carbon–carbon bond in C_2F_4 has already been noted.[8] In order to acount for it, it has been suggested that, near the minimum of its ground electronic state, C_2F_4 is "attempting" to dissociate into two excited CF_2 biradicals in their lowest triplet states, $^3B_1$.[8] The potential-energy curve relating to the approach of two singlet, unexcited CF_2 molecules ($^1A_1$) must be repulsive, since their dimerisation proceeds so slowly. Because the ground-state products lie lowest in energy, this curve must cross that which correlates with the two triplet biradicals, is shown in Figure 3. This crossing cannot occur in C_2H_4 if the ground state of CH_2 is the (linear) triplet.[22] The transition state in the association of two unexcited CF_2 molecules, or the dissociation of C_2F_4 in its ground electronic state, corresponds to the crossing of the two potential-energy curves correlating with normal ($^1A_1$) and excited ($^3B_1$) CF_2. The dissociation energy $D(F_2C\text{–}CF_2)$ is reduced relative to $D(H_2C\text{–}CH_2)$ by about twice the energy of CF_2 ($^3B_1$) above its ground state (assuming that the dissociation of C_2F_4 into two triplet carbenes requires ~160 kcal./mole as in C_2H_4). This places CF_2 ($^3B_1$) ~45 kcal./mole above CF_2 ($^1A_1$), and if CF_2 ($^1B_1$) does lie at 108 kcal./mole (4·7 ev) the singlet–triplet splitting of the B_1 levels is ~60 kcal./mole.

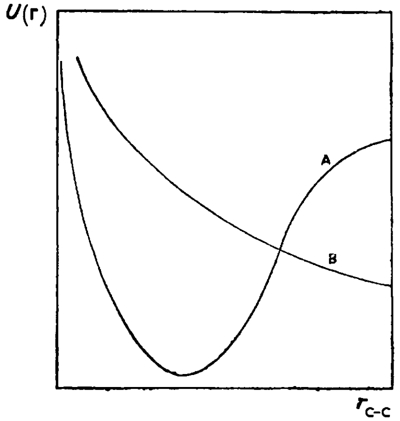

FIGURE 3. Potential-energy curves in C_2F_4
A, $CF_2(^3B_1) + CF_2(^3B_1)$;
B. $CF_2(^1A_1) + CF_2(^1A_1)$

In CCl_2 and CBr_2, it is to be expected that the splitting between the mean energy of the $^3B_1$ state and the corresponding $^1B_1$ state will fall (although the increased spin–orbit

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[26] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd edn., Butterworths, London, 1958.

[27] R. I. Reed and W. Snedden, *Trans. Faraday Soc.*, 1958, **54**, 301.

[28] O. Ruff and H. Wallauer, *Z. anorg. Chem.*, 1931, **196**, 421.

[29] R. C. Petry and J. P. Freeman, *J. Amer. Chem. Soc.*, 1961, **83**, 3912.

coupling will separate the three components of the $^3B_1$ level more widely). The poorer p_π overlap between the carbon and the heavier halogen atoms, together with their smaller electronegativity, results in greater localisation of the $2b_2$ orbital on the carbon atom. Since electrons in the $4a_1$ orbital also tend to be localised on the carbon atom, the separation of electrons which takes place in the triplet state will be restricted, and the stabilisation of the $^3B_1$ level will be reduced. At the same time, the $^1B_1$–$^1A_1$ separation should also fall, since the electrons in the $4a_1$ level will be less tightly bound in CCl_2 and CBr_2. In consequence, the separation between the $^3B_1$ and $^1A_1$ levels should not change greatly. If the dissociation of C_2Cl_4 and C_2Br_4 can be represented by the potential-energy curves of Figure 3, their dissociation energies at the central bond should also be low and comparable to that in C_2F_4. Similar arguments will apply to mixed ethylenes such as $CF_2{:}CCl_2$ or $CF_2{:}CBr_2$; an interesting case is $CF_2{:}CH_2$, which should have a dissociation energy midway between those of C_2F_4 and C_2H_4.[8]

To summarise, it is suggested that dimerisation of the halogenocarbenes requires the promotion of electrons from the $4a_1$ into the $2b_1$ orbital. These are directed along, and at right angles to, the molecular symmetry axis, respectively. The resulting biradicals will attract each other, to produce one σ- and one π-carbon–carbon bond, whose equilibrium length and force constant are appropriate to a double bond. The sluggish dimerisation of CF_2 ($^1A_1$) can be attributed to the high energy required to excite the electrons into the $^3B_1$ valence state. The reverse reaction is aided by the energy released on reorganisation of the carbene into the more strongly bound ground state.

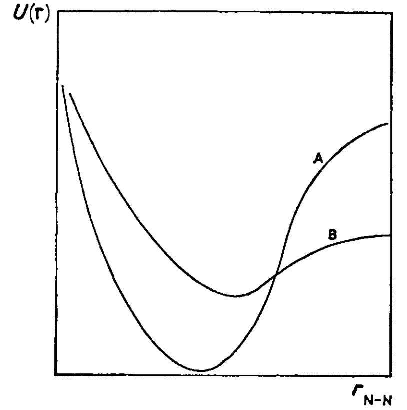

FIGURE 4. Potential-energy curves in N_2F_4
A, $NF_2(^2A_1) + NF_2(^2B_1)$;
B, $NF_2(^2B_1) + NF_2(^2B_1)$

The dissociation of N_2F_4 and dimerisation of NF_2 can be described in similar terms. In the ground state of the NF_2 radical, the odd electron residues in the $2b_1$ orbital, perpendicular to the molecular plane. The approach of two of the radicals in their ground electronic states could result only in the formation of a weak N–N π-bond; no σ-interaction would be possible, since the $4a_1$ orbitals are doubly occupied. A much stronger bond will be formed if an electron in one of the radicals is promoted from the $4a_1$ into the $2b_1$ orbital; this will permit the formation of an N–N σ-bond, through overlap of the $4a_1$ and $2b_1$ orbitals. The product will be non-planar, as found experimentally.[30]

The association of two NF_2 radicals may be represented on a potential-energy diagram as in Figure 4; the formation of the N–N bond has to be " paid for " by the excitation of an electron out of the tightly bound $4a_1$ orbital. As in C_2F_4, this results in a drastic reduction of the N–N bond strength, while the bond length remains short. In the NH_2 radical, the corresponding electron promotion requires much less energy, since the outermost a_1 level is much less tightly bound. The dimerisation of NH_2 occurs readily[31] and the N–N bond strength in N_2H_4 is nearly three times that in N_2F_4.[6,7]

[30] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 1959, **31**, 1129.
[31] M. H. Hanes and E. J. Bair, *J. Chem. Phys.*, 1963, **38**, 672.

(b) *Other reactions.* Bimolecular reactions of CF_2 ($^1A_1$) may be separated into two categories, namely, those in which the approaching species has its outermost molecular orbital either singly or doubly filled. In the former case, the reaction is with a free radical (or radical-like species such as oxygen), and in the latter case with a two-electron donating molecule such as an olefin. Reactions with free radicals will be relatively slow at normal temperatures, since the odd electron will have to be placed in the $2b_1$ orbital of the CF_2, high on the energy scale and C–F antibonding. The rate of decay of CF_2 ($^1A_1$) produced through flash photolysis of CF_2Br_2 is unaffected by addition of a large excess of oxygen.[1]

In its molecular reactions, for example, insertion into the π-bond of an olefin, CF_2 ($^1A_1$) should behave as an electrophilic reagent, since its carbon atom is electron-deficient. However, the deficiency is partially relieved by the π-overlap with the $2p_F$ orbitals, which must hinder acceptance of a pair of electrons. The addition of CF_2 ($^1A_1$) to an olefin should be very slow in comparison with CH_2 ($^1A_1$), where the empty orbital is low-lying and not involved in π-bonding. Addition will be accelerated by substitution of electron-releasing groups in the olefin. This has been demonstrated experimentally for CCl_2 [32] and CBr_2,[15] but quantitative data for CF_2 are not yet available; Fielding and Pritchard could detect no reaction with ethylene at 250°C.[33] CCl_2 was found to be more discriminating than CBr_2, consistent with the view that the π-overlap would become less pronounced in the series $CF_2 > CCl_2 > CBr_2$.

Addition of CF_2 to I_2 and HCl [34,3] at elevated temperatures has been reported, the activation energy of the latter being ~6 kcal./mole. Its course may be represented by the sequence where electrons in a non-bonding $3p$ orbital on the Cl atom are donated initially into the $2b_1$ orbital of the CF_2.

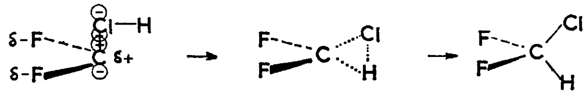

FIGURE 5. Transition states in the reaction: $CF_2 + HCl \longrightarrow CF_2HCl$

Reaction of NF_2 in its ground state is hampered by its having its odd electron in the $2b_1$ π-orbital. This is apparent in the slow rate of dimerisation, and also in the very weak bond formed when it reacts with NO. Like NF_2, the odd electron in the ground electronic state of NO ($^2\Pi$) is also in an antibonding π-orbital; addition of one to the other can only produce an extremely weak π_{N-N} bond. In order to produce the much stronger σ_{N-N} bond, it will be necessary once more to promote a $4a_1$ electron in the NF_2 into the $2b_1$ orbital. Excitation of an electron in NO will require a greater energy. Just as in N_2F_4, the product will be a bent molecule with a low N–N bond strength; it is, in fact, ~10 kcal./mole.[35] The stronger N–N bond that is produced only just compensates for the high energy required to promote the electron out of the $4a_1$ orbital.

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