followed by eq. 6. Approximate calculations of ΔH show that eq. 9 and 10 are the favored reactions despite the weakness of the O–N bond ($\sim$35 kcal.)[27] relative to the S–O ($\sim$65 kcal.)[27] and C–O ($\sim$81 kcal.) bonds. Rupture of the O–N bond would lead to SOF_4 (or COF_2) and NF_3. None of the latter compounds was obtained. A higher temperature is required for the decomposition of CF_3ONF_2 than for SF_5ONF_2 because of the greater strength of the C–O bond relative to the S–O bond.

Acknowledgments.—We wish to thank Mr. James A. Ferretti for his assistance with the calculated and experimental n.m.r. spectra. W. H. H. appreciates the financial assistance given by the Standard Oil Company of California.

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Molecular Structure and Bonding of $N_2(CF_3)_4$. An Electron Diffraction Study[1,2]

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The molecule $(CF_3)_2NN(CF_3)_2$ represents an interesting example in which, paradoxically, a bond appears to be strengthened and shortened by virtue of strong nonbonded repulsions across it. The substance has been reported to be exceptionally stable to thermal decomposition, and its central N–N bond was observed in this study to be perhaps 0.05 Å. shorter than its counterpart in N_2H_4. The crowding of trifluoromethyl groups is found to flatten the two $>$N– pyramids almost to planarity and to set the dihedral angle between opposite $-N(CF_3)_2$ groups at a value of about 90°. A molecular orbital description suggests that the short N–N bond may be understood in terms of the enhancement of π bonding ensuing from the nearly D_{2d} symmetry imposed by steric forces. Structural parameters and amplitudes of vibration of the free (gaseous) molecules were determined by electron diffraction. All bond lengths except for N–N were found to be normal. The large deformations from normal bond angles lead to a rather efficient solution of the molecule's steric problems. Nonbonded repulsions are not borne by a few highly compressed atoms but are distributed among two dozen atom pairs in normal van der Waals contact.

Introduction

The compound tetrakis(trifluoromethyl)hydrazine poses several interesting questions. It has been reported by Young and Dresdner[3] to be enormously more stable to the thermal rupture of its N–N bond than a number of other hydrazine derivatives. Its stability is even more remarkable when it is considered that it is among the most crowded of the derivatives studied and must suffer substantial repulsions between its bulky CF_3 groups. If the molecule were assumed to have normal bond lengths and to have bond angles similar to those of hydrazine itself, the implied nonbonded $F\cdots F$ distances would be almost 1 Å. shorter than any nongeminal $F\cdots F$ distances ever observed. Since such short distances are highly improbable it seemed worthwhile to investigate the deformations in structure introduced by steric stress. It was hoped that a structural analysis might also shed light on the surprising stability of the substance.

Experimental

A sample of $N_2(CF_3)_4$ was donated by Professor John A. Young. Gas phase chromatography indicated that the compound was approximately 99% pure. Diffraction patterns were taken with the Iowa State University sector electron diffraction apparatus[4] using a sample pressure of 15 torr. Absorbancies of diffraction patterns were converted to intensities in a manner described elsewhere.[4-6]

Structure Analysis

Leveled experimental intensities $I_0(q)$ were converted to reduced molecular intensities by the procedure outlined in ref. 6. The leveled intensities and associated background functions are shown in Figure 1. Experimental radial distribution functions, incorporating a modification function $\exp(-0.00166s^2)$, were calculated using theoretical data for the range $q = 0$ to $q = 16$ and experimental data for $q = 17$ to $q = 120$.

The experimental distribution curves bore scant resemblance to a variety of initial synthetic curves calculated for plausible molecular parameters. Therefore it was decided to make some rather severe simplifying assumptions about the structure and to optimize parameters before relaxing the assumptions.

It is reasonable to expect the present molecule to have C_2 symmetry and, accordingly, 25 independent structural parameters. If all C–F bonds are assumed to have the same length, all C–N bond lengths are taken

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(1) This research was supported by a grant from the National Science Foundation.

(2) Based in part on a dissertation by H. K. Higginbotham to the Graduate School, Iowa State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1964.

(3) J. A. Young and R. D. Dresdner, *J. Org. Chem.*, **28**, 833 (1963).

(4) L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *J. Chem. Phys.*, **35**, 1211 (1961).

(5) L. S. Bartell and L. O. Brockway, *J. Appl. Phys.*, **24**, 656 (1953).

(6) R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

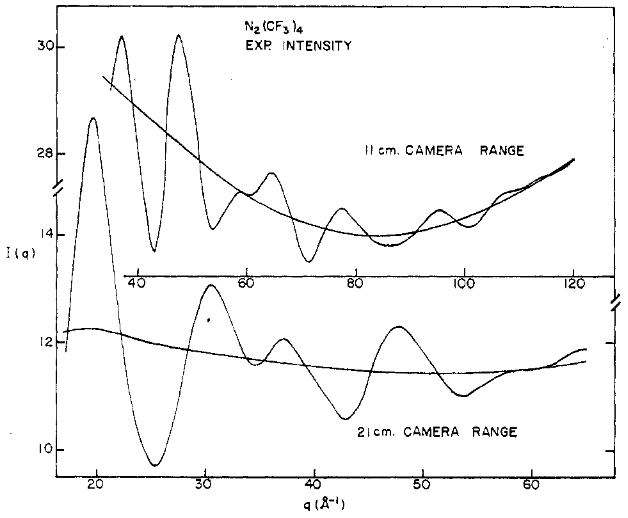

Figure 1.—Experimental intensity and background functions for $N_2(CF_3)_4$.

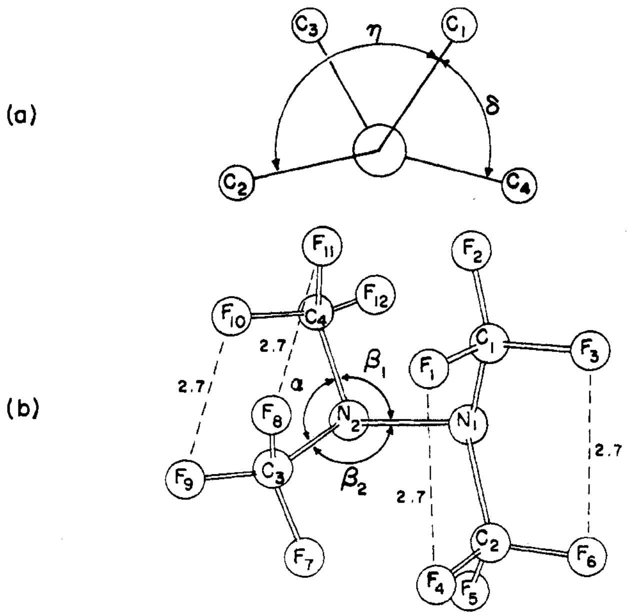

Figure 2.—Identification of molecular parameters in $N_2(CF_3)_4$.

as equal, and all FCF angles are considered identical, the number of structure parameters needed to specify the structure is reduced to 14. This is still an excessive number to handle simultaneously in gas diffraction, so the following restrictions, pertaining to variables identified in Figure 2, were incorporated into "model R."

Model R restrictions: (1) molecule has C_2 symmetry; (2) all C–N bond lengths are equal; (3) all CF_3 groups possess threefold symmetry and identical bond lengths and angles; (4) axes of CF_3 groups coincide with C–N bonds; (5) β_1 equals β_2; (6) dihedral angle δ equals $\eta/2$; (7) $F_3C\text{–}N\text{–}CF_3$ groups have C_{2v} symmetry and their component bonds exhibit normal staggering.

Model R has only six freely variable structure parameters. A complete radial distribution function is determined by these parameters together with many more than six amplitudes of intramolecular vibrations. It is not possible to establish all atom pair amplitudes uniquely but a reasonable set may be deduced experimentally.

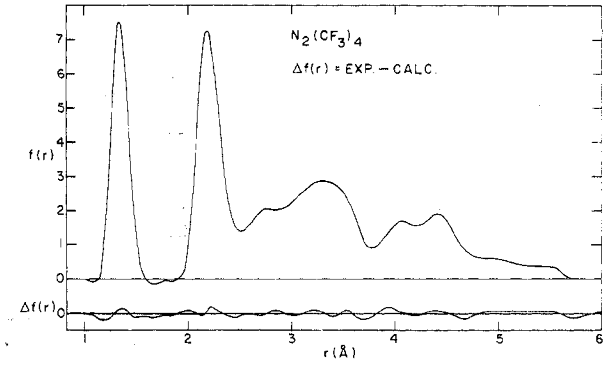

Figure 3.—Experimental radial distribution curve for $N_2(CF_3)_4$ (upper figure). Difference between experimental and calculated radial distribution (lower figure).

After considerable trial and error coupled with least-squares analyses of fragments of the curves, a model R structure evolved which gave a synthetic radial distribution function in rather good agreement with experiment. The experimental curve and its deviation from the best model R synthetic curve are illustrated in Figure 3. Molecular parameters corresponding to this model are listed in Table I along with rough estimates of probable errors. No great quantitative significance should be attached to the uncertainties as they largely neglect the possible influence of relaxing the restrictions of model R. Bond angles were not corrected for shrinkage effects.

Also listed in Table I are results of a few trials in which individual restrictions of model R have been relaxed. No models were found which gave an appreciably better fit with experiment than model R itself.

TABLE I

STRUCTURAL PARAMETERS AND ROUGH ERROR ESTIMATES FOR $N_2(CF_3)_4$ (DISTANCES IN Å.)

(I) Analysis Subject to the Constraints of Model R[a]

Bond	Mean lengths, r_g	Mean amplitudes, l_g
N–N	$1.40_2 \pm 0.02$	(0.05) assumed
C–N	$1.43_3 \pm 0.01$	0.041 ± 0.008
C–F	$1.32_5 \pm 0.005$	0.042 ± 0.005

$\angle CNC = 121.2 \pm 1.5°$ $\angle FCF = 108.2 \pm 0.5°$

$\angle NNC = 119.0 \pm 1.5°$ $\eta = 170 \pm 5°$[b]

dihedral angle $\delta = \eta/2$ (assumed)[b]

(II) Analysis with Constraints of Model R Partially Relaxed

Constraint relaxed[a]	Conclusion
(5)	Fit worsened if β_2 differs from β_1 by more than 2.5°
(6)	$\delta = 88 \pm 4°$

[a] See text for listing of constraints imposed in analysis. [b] See Figure 2 for identification of parameter.

Restrictions (1), (2), and (3) probably do not introduce limitations of consequence into the analysis. Restriction (4) is unlikely to be satisfied precisely, however. Deviations of CX_3 group axes from bond axes of two or three degrees have been observed for methyl

TABLE II

STRUCTURAL PARAMETERS FOR $N_2(CF_3)_4$ AND RELATED COMPOUNDS

Molecule	NN, Å.	CN, Å.	CF, Å.	∠NNC, deg.	∠CNC, deg.	∠FCF, deg.	Method
$N(CH_3)_3$		1.47 ± 0.01			108 ± 4		VED[a]
$N(CF_3)_3$		1.43 ± 0.03	1.32 ± 0.03		114 ± 3	108.5 ± 2	VED[b]
N_2H_4	1.47 ± 0.02						VED[c]
	1.453 ± 0.005						IR[d]
	1.449 ± 0.004						MSED[e]
$N_2H_2(CH_3)_2$	1.45 ± 0.03	1.47 ± 0.03		110 ± 4	110 ± 4		VED[f]
$N_2(CF_3)_4$	1.40 ± 0.02	1.433 ± 0.01	1.325 ± 0.005	119.0 ± 1.5	121.2 ± 1.5	108.2 ± 0.5	MSED[g]

[a] Visual method, electron diffraction: L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.*, **58,** 2036 (1936). V. Schomaker, quoted in "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, Burlington House, W.I., London, 1958. [b] R. L. Livingston and G. Vaughan, *J. Am. Chem. Soc.*, **78,** 4866 (1956). [c] Reference 11. [d] Infrared method, ref. 12. [e] Microphotometer-sector method, electron diffraction; ref. 13. [f] W. Beamer, *J. Am. Chem. Soc.*, **70,** 2979 (1948). [g] Present investigation.

groups in several compounds,[7] and deviations in crowded molecules such as $N_2(CF_3)_4$ might conceivably be larger. Restriction (5) has been found not to hold in the similar compound N_2F_4 where β_1 and β_2 differ by several degrees according to preliminary analyses by Bauer and Bohn.[8] Although a corresponding deviation might apply to the present molecule, the structure found for $N_2(CF_3)_4$ is distorted in such a way as to reduce greatly any electronic distinction between β_1 and β_2. In fact, the distinction would vanish altogether in the limit of D_{2d} symmetry which is approached by $N_2(CF_3)_4$. Some evidence exists that δ slightly excessed $\eta/2$ as indicated in Table I.

The polymer Teflon has $CCF_2CF_2CF_2C$ chains analogous to the FCF_2NCF_2F groups in $N_2(CF_3)_4$. Teflon chains deviate from restriction (7) by following a gentle (sterically induced) helical twist[9] rather than a C_{2v} planar zigzag of the type found in *n*-hydrocarbons.[10] A Teflon twist in $N_2(CF_3)_4$ is not excluded by the diffraction data. The steric environment in the hydrazine implied by the present analysis would seem to reduce any advantage of a Teflon-like twist.

It is uncertain to what extent small details in the molecule are misrepresented owing to the necessary simplifications of the analysis. On the other hand, it is unlikely that the general features reported for the structure will be found to be in error.

Results

Bond Lengths and FCF Angles.—Structural parameters in $N_2(CF_3)_4$ are compared with those of related molecules in Table II. The CF_3 groups in the substituted hydrazine are very similar to CF_3 groups encountered in other molecules (including $N(CF_3)_3$ in Table II). The C–N bonds in the CF_3 derivative are slightly shorter than in compounds with CH_3 groups, in keeping with the usual trend. Differing significantly from the corresponding bond in hydrazine is the N–N bond. It was found to be 0.05–0.07 Å. shorter than in N_2H_4.[11–13]

Dihedral Angles.—Information on dihedral angles in hydrazine derivatives is very meager. Dihedral angles in substituted ethanes, of course, are approximately 60 or 180°. In H_2O_2 the corresponding angle seems to be approximately 120°.[14] It would appear that the dihedral angle of nearly 90° in $N_2(CF_3)_4$ is dictated in large measure by the crowding in the molecule. Nevertheless, it is not greatly different from the angle of about 90° provisionally reported for N_2H_4[12] and for the somewhat analogous case of O_2F_2.[15]

Nonbonded Distances.—The reasonableness of the bond lengths inferred and the neat way the bulky groups are found to fit together in model R lend some confidence in the structural parameters deduced, despite the severe constraints of the model.

The CF_3 groups on the same side of the N–N bond adjust to achieve a normal 2.7 Å. distance between fluorines ($F_3 \cdots F_6$ and equivalent) as shown in Figure 2b. In model R the $F \cdots F$ interactions across the N–N bond are 0.2 Å. or more in excess of the van der Waals diameters.[16] This ample clearance should not be taken to signify that the groups at opposite ends of the molecule are packed loosely together. The firmest contacts are apparently made between carbons ($C_1 \cdots C_3$, $C_1 \cdots C_4$, $C_2 \cdots C_3$ at 0.15 Å. less than van der Waals sums),[17] between $C \cdots F$ pairs ($C_2 \cdots F_7$, $C_4 \cdots F_2$ at normal van der Waals separation), and between $N \cdots F$ pairs ($N_1 \cdots F_{12}$, $N_1 \cdots F_7$, and equivalent).[18] The latter $N \cdots F$ distances in model R are about 0.2 Å. closer than normal van der Waals separations, suggesting that the CF_3 group axes may actually be tipped somewhat out of line with the C–N bonds. Counteracting this tipping, however, are the $F_1 \cdots F_4$, etc. (close-packed at the normal 2.7 Å. distance), and the very tight $C_1 \cdots F_4$ and equivalent distances (at about 0.15 Å. less than normal van der Waals sums).[17]

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[7] E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, **21,** 1804 (1953); T. Nishikawa, T. Itoh, and K. Shimoda, *ibid.*, **33,** 1735 (1955); T. Kojima, *J. Phys. Soc. Japan*, **15,** 1284 (1960).

[8] S. H. Bauer and R. K. Bohn, private communication.

[9] C. W. Bunn and D. R. Holmes, *Discussions Faraday Soc.*, **25,** 95 (1958).

[10] C. W. Bunn, *Trans. Faraday Soc.*, **35,** 482 (1939).

[11] P. A. Giguere and V. Schomaker, *J. Am. Chem. Soc.*, **65,** 2025 (1943).

[12] A. Yamaguchi, I. Ichishima, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **31,** 843 (1959).

[13] Y. Morino, T. Iijima, and Y. Murata, *Bull. Chem. Soc. Japan*, **33,** 46 (1959).

[14] R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, **36,** 1311 (1962).

[15] R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

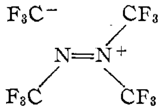
[16] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 260.

[17] Based on carbon radius of 1.7 Å. The effective van der Waals radius in CF_3 might be slightly smaller (as is the bond radius).

[18] Note that Figure 2b is schematic, being drawn on the basis of normal hydrazine bond angles, and therefore overemphasizes the heights of the N-atom pyramids in $N_2(CF_3)_4$. Consequently, the figure is somewhat misleading in picturing the nonbonded distances discussed in this section.

It would appear that the molecule achieves a rather efficient solution of its steric problems by its bond angle deformations. Nonbonded repulsions are not borne by a few highly compressed atoms but are distributed among two dozen atom pairs in essentially normal van der Waals contact.

Bond Deformations.—Most notable among the molecular features found are the flatness of the –N< pyramids and the apparent shortness of the N–N bond. The flatness greatly exceeds that reported in other small saturated amine derivatives and is undoubtedly due in part to the large steric stress introduced by the bulky CF_3 groups. Since this strain would of itself certainly not lead to a shortening of the N–N bond, and since the flattening is much greater than in $N(CF_3)_3$, it may be appropriate to invoke resonance forms of the type



etc., not suitable for $N(CF_3)_3$ or methyl derivatives. At first glance this resonance form with its implied π bond across the N–N bond seems at variance with the nonplanarity of the σ framework (almost a 90° twist!). It emerges, however, that the 90° twist induced by steric deformation actually enhances rather than reduces the π character and concomitant shortening of the N–N bond. This is more readily discussed in terms of a molecular orbital than a valence bond description.

Discussion

MO Description of Bonding.—Let us consider only the N_2C_4 framework and construct MO's from the nitrogen 2s and 2p orbitals and from the tetrahedral carbon hybrid orbitals directed toward the nitrogens. Out of these 12 AO's can be constructed 12 MO's into which 14 valence electrons must be placed. In the limit of D_{2d} symmetry (90° twist of planar C_2N–N groups) the electron configuration is given by[19-21]

$$(NN)_{a_1}{}^2(CN)_{a_1}{}^2(CN)_{b_2}{}^2(CN)_e{}^4(n)_e{}^4$$

in which a_1 and b_2 orbitals (identified by their symmetry type and, loosely, by their principal bonding roles) utilize the N–N σ orbitals and symmetric[22] combinations of carbon orbitals. Six electrons in these nondegenerate orbitals account for the N–N σ bond and half of the C–N σ bonding. The doubly degenerate orbitals, which hold the key to the problem, are each constructed from nitrogen pπ orbitals and the antisymmetric[22] combination of carbon orbitals. In a given plane the three MO's, which resemble those for the allyl π system, are shown schematically in Figure 4.

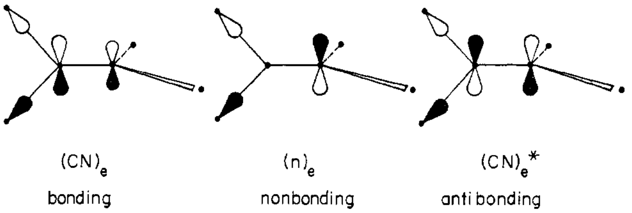


Figure 4.—Schematic representation of the molecular orbitals contributing to the N–N π bond order for D_{2d} symmetry.

The e orbital of lowest energy is bonding not only for C–N pairs (four electrons providing the remaining half of the C–N σ bonds) but also for the N–N pair. The last populated π orbitals are the essentially *nonbonding* $(n)_e$ orbitals. It is readily seen that the MO description exhibits features similar to those of the valence bond resonance structure invoked above in implications of charge distribution and N–N π bonding. Nitrogen "lone-pair" electrons, populating the $(n)_e$ orbitals, are strongly delocalized onto the carbons. This and the approximately equal role played by carbon and nitrogen orbitals in the combinations of Figure 4 are reasonable because of the high electronegativity of the CF_3 groups.

Unstrained hydrazine derivatives X_2N–NX_2 presumably have C_2 symmetry. Their structures may be derived from a D_{2d} structure by one or both of the following deformations: (a) a twist from D_{2d} toward D_{2h} (planar); (b) a bending of the X_2N planes away from the N–N axis. A molecular orbital treatment leads to quite definite implications about the influence of deformations (a) and (b) on the N–N π bonding character.[23] Warping the D_{2d} structures removes the degeneracy of the e-type π orbitals and, in the case of deformation (b), introduces some N–N σ character into them. The purely bonding nature of the $(CN)_e$ π orbitals is partially lost as the symmetry is lowered. An antibonding component mixes with one or both of the orbitals, depending upon the kind of distortion. The deformed $(n)_e$ orbitals retain their role of accommodating the "lone-pair" electrons and, if completely filled, remain essentially nonbonding in net effect. One of the orbitals becomes bonding as the nuclei are displaced but the other compensates by acquiring an antibonding aspect. The remaining (unpopulated) antibonding $(CN)_e{}^*$ functions as a pair become less severely antibonding for the N–N bond. Deformation (b) adds a certain amount of N–N π character to the orbitals derived from D_{2d} a_1- and b_2-type orbitals. The resultant C_2 A- and B-type orbitals have opposite bonding characteristics and virtually cancel each other's π bond order.

The influence of symmetry may be summarized as follows. Among the configurations studied, D_{2d} most effectively apportions the *bonding* π character to the lowest energy orbitals and the *antibonding* to the highest. Deformations from D_{2d} tend to scramble the N–N π bonding and antibonding components among the levels. Now, the Coulson π bond order for N–N would

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[19] R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932); *ibid.*, **43**, 379 (1933); *J. Chem. Phys.*, **3**, 517 (1935).

[20] R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947); R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

[21] W. Moffitt and J. Scanlan, *Proc. Roy. Soc.* (London), **A218**, 464 (1953).

[22] With respect to 180° rotation about the N–N axis.

[23] In this structural paper it seems inappropriate to give an account of details of the straightforward MO treatment. The trends in bond order are derivable by inspection and stem essentially from symmetry considerations.

be zero for *any* symmetry if all orbitals were filled. In the hydrazine derivative all but the highest pair of nominally π orbitals are filled. Therefore, the greatest Coulson π order will belong to the configuration which maximizes its antibonding character in the top pair of orbitals.[24]

A related situation is encountered in ethylene. With two fewer electrons, the molecule escapes the necessity of using the D_{2h} antibonding orbitals correlated with $(n)_e$ and preferentially adopts the double-bonded planar configuration. Rotation to D_{2d} symmetry (90°) does not wholly destroy the double bond, however. As was pointed out by Mulliken over 30 years ago,[19] π electron delocalization into the orbitals illustrated in Figure 4 makes the C–C bond in the singlet state of the 90° configuration approximately 1 volt more stable than it would be otherwise. This estimate has stood the test of more recent theoretical investigations.[20] The excess stabilization may be thought of as a form of hyperconjugation.

Finally, it may be noted that "steric *inhibition* of resonance" is often invoked in descriptions of sterically perturbed π electron systems such as *ortho*-substituted nitrobenzenes.[25] The situation in $N_2(CF_3)_4$ is somewhat analogous but the greater number of π electrons per bond leads, as it were, to a "steric *enhancement* of resonance."

Relation to Stability.—A shortening of the N–N bond by 0.05 Å. does not signify any enormous stabilization of the bond. Various empirical relations[26] indicate that such a shortening corresponds to an increase in bond energy of roughly 10 kcal./mole. It is not clear how much of this would be reflected in the activation energy for bond rupture.

In evaluating the proposed steric-covalent coupling scheme it should be taken into account that bonds to nitrogen are sensitive to substituents in a way that is imperfectly understood. When H atoms in H_2NNH_2 are replaced by CH_3 groups, the N–N dissociation energy decreases,[27] showing that a modest increase in substituent bulk does not cause steric enhancement of stability. Since the substance N_2F_4 has a particularly low dissociation energy,[3,28] it is apparent that high substituent electronegativity does not in itself stabilize the N—N bond. This correlation may be deceptive, however, for increasing the electronegativity of X in molecules of the formula $X{-}N{=}O$ has the effect of shortening and stiffening the $N{=}O$ bond.[29] Moreover, FOOF, a close analog of F_2NNF_2, has a surprisingly short O—O bond and long O—F bonds.[30] These electronegativity effects can be accounted for by resonance forms $X^-N{=}O^+$ and $F^-O{=}O^+{-}F$, etc., which are closely related to the form invoked above for $N_2(CF_3)_4$. The fact that the N—N bond in N_2F_4 is weak despite the electronegativity effect has been explained by Kaufman[31] on the basis of a special stability of the dissociation products, NF_2 radicals.

The bond tightening in $N_2(CF_3)_4$ may stem in part, then, from the high electronegativity of CF_3 groups. The point we stress is that the tightening should be augmented by the steric-covalent coupling mechanism discussed in the foregoing.

It is difficult to assess accurately the contribution of the large number of van der Waals contacts across the N–N bond. At the cost of substantial deformation of bond angles, many of the compressed atoms are at a distance where the *force* is still repulsive but the *potential energy* is negative (*i.e.*, stabilizing). Therefore, the nonbonded interactions may play a role in molecular stability over and above that of enhancing π bonding. If, contrary to reality, the nonbonded potential energy functions were monotonic and positive (*i.e.*, repulsive at all distances) a steric deformation to D_{2d} presumably would still shorten the N–N bond and conceivably could increase the activation energy for dissociation. A deformation induced by such purely repulsive interactions could not, however, increase the *thermodynamic* stability with respect to dissociation without violating the first law.

It is prudent to regard the exact length of the N–N bond in this investigation as uncertain in view of the complexity of the analysis and the simplifications which had to be imposed.[32] It is not proven that the observed shortening and stability are closely related or, for that matter, that either observable is related to the skeletal symmetry in the manner suggested by the molecular orbital picture. Nevertheless, it is appealing, if speculative, to make the connection and to draw attention to the paradoxical strengthening and shortening of the central bond seemingly resulting from the strong nonbonded repulsions across it.

Acknowledgments.—We wish to thank Professor J. A. Young for supplying us with a sample of $N_2(CF_3)_4$ and calling our attention to its properties. We are also pleased to acknowledge the great assistance of Mr. Nicholas Magnani in some phases of the structure analysis.

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[24] Since the completion of this manuscript Dr. Roald Hoffmann has carried out a series of calculations for $N_2(CH_3)_4$ using his extended Hückel molecular orbital method which takes into account all valence orbitals of all atoms [*J. Chem. Phys.*, **39**, 1397 (1963)]. The cases of D_{2d} symmetry and a variety of deformations from D_{2d} were considered. The results of this more elaborate treatment confirmed the principal conclusions of the present paper in singling out D_{2d} symmetry for maximum charge on the carbon atoms, minimum charge on the nitrogens, and maximum N–N bond order (private communication, 1965).

[25] G. W. Wheland, "Resonance in Organic Theory," John Wiley and Sons, Inc., New York, N. Y., 1955.

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[27] J. A. Kerr, R. C. Sekhar, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3217 (1963).

[28] C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960); J. T. Herron and V. H. Dibeler, *ibid.*, **35**, 747 (1961); L. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *ibid.*, **35**, 1481 (1961).

[29] H. W. Brown and G. C. Pimentel, *ibid.*, **29**, 883 (1958); W. G. Burns and H. J. Bernstein, *ibid.*, **18**, 1669 (1950); Y. Y. Kharitonov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1953 (1962); D. J. Millen and J. Panell, *J. Chem. Soc.*, 1322 (1961); L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

[30] R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

[31] J. Kaufman, *Chem. Eng. News*, **43**, No. 17, 47 (1965).

[32] It may be remarked that, at the time of the structure analysis, the possible connection between the N–N bond order and distorted structure had not been recognized. If a prejudice existed to bias the analysis, it was in the direction of lengthening rather than shortening the bond. The apparent shortness of the N–N bond was considered a disagreeable anomaly which refused to drop out of the analysis as refinements progressed.