[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

An Electron Diffraction Investigation of the Structure of Difluorodiazine

BY S. H. BAUER

Introduction

When one considers the compounds which could be formed between nitrogen and fluorine, our limited experience suggests the following four: NF_3, N_2F_2, N_2F_4 and N_3F. Compounds of higher molecular weight would require nitrogen chains involving more than three such atoms, and to our knowledge, attempts to prepare longer chains of nitrogen atoms have not been successful.

Fortunately, small samples of fluorine azide and difluorodiazine were available to us for structure determination; tetrafluorohydrazine and nitrogen trifluoride were not. However, the structure of the latter has been established. The infrared absorption spectrum of nitrogen trifluoride was first obtained by Bailey, *et al.*,[1] who made a provisional assignment of the observed fundamental frequencies. The molecular symmetry is C_{3v}; and the N–F separation, as deduced from the force constant of 0.410 megadynes/cm. by means of Badger's rule, is 1.45 Å.; the ∠FNF is 110° or somewhat larger. Dr. V. Schomaker communicated to us his electron diffraction results on NF_3: N–F 1.37 ± 0.02 Å.; ∠FNF 102.5 ± 1.5°. We thank him sincerely for these data.

Remarks Regarding the Materials Available

In contrast with nitrogen trifluoride, which has been known for more than eighteen years,[2] fluorine azide and difluorodiazine have been prepared only recently by Haller working under the direction of Professor A. W. Browne[3]; the former by treating in a stream of nitrogen, hydrazoic acid with fluorine, for which they suggest as the most probable reaction

$$4HN_3 + 2F_2 = NH_4F + N_2 + 3N_3F$$

and the latter compound through the decomposition of the fluorine azide, according to the reaction

$$2N_3F = 2N_2 + N_2F_2$$

The following characteristics of the compounds are quoted from Haller's dissertation. "Fluorine azide is a greenish-yellow gas at ordinary temperatures; it liquefies at −82° when distilled with nitrogen, and freezes to a greenish-yellow solid at −154°. When the liquid is vaporized, explosion generally occurs. In the gas phase, at pressures under 200 mm., N_3F decomposes, slowly at room temperature and very rapidly near the boiling point of water, to produce nitrogen and N_2F_2. "At ordinary temperatures difluorodiazine is a colorless stable gas with an odor like NO_2. It condenses to a colorless solid at about −110° (v.p. 100 mm.)."

Only qualitative analyses were made on either compound; both were shown to consist of nitrogen and fluorine only. Upon removal of the excess nitrogen, molecular weights were determined. For N_3F (61), 61.6 and 62.5 were found, while for N_2F_2 (66), 66.2 and 68.0 were obtained. The high values in both instances were accounted for by assuming slight contaminations—in the case of N_3F with N_2F_2, since it was practically impossible to avoid some decomposition in spite of the rapidity of the measurements, and in the case of N_2F_2 with NF_3, probably introduced through the action of excess fluorine on the fluorine azide; thus

$$N_3F + F_2 = NF_3 + N_2$$

In interpreting the electron diffraction data, these complications had to be taken into consideration.[4] The author is greatly indebted to Dr. Haller for the samples of N_3F and N_2F_2, and for aid in handling the compounds.

The Electron Diffraction Photographs

Fluorine Azide.—Diffraction photographs were taken of a freshly prepared sample (kept at about −78°, at a pressure of 150 mm.). Although the contents of bulb were distinctly greenish-yellow at the beginning of the run, twenty minutes later the color had faded considerably. The resulting patterns were all alike, and were qualitatively indistinguishable from those obtained when electrons were diffracted by N_2F_2, whereas a comparison of the theoretical curves for the most probable structures indicated that a large difference should be observed. We therefore concluded that the brass tube leading from the sample flask to the nozzle probably catalyzed the conversion of the unstable fluorine azide to the more stable difluorodiazine."

Difluorodiazine.—Photographs were taken on Eastman Kodak Co. Commercial plates of a sample kept at room temperature, under an initial pressure of 81 mm. The accelerating potential was 43.76 KV, and the nozzle-plate distance 19.12 cm. Five maxima were observed; the general appearance of the photographs is as sketched in Fig. 1 (V); it is indeed doubtful whether the slight shoulder to the right of the fourth maximum is real; subsequent study of the photographs convinced us that this peak is somewhat broader than the others, but is essentially symmetrical. No

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[1] C. R. Bailey, J. B. Hale and J. W. Thompson, *J. Chem. Phys.*, **5**, 275 (1937).

[2] O. Ruff, J. Fischer and F. Luft, *Z. anorg. Chem.*, **172**, 417 (1928).

[3] J. F. Haller, Doctoral Dissertation, Cornell University, September, 1942.

[4] Assuming NF_3 to be the sole impurity in the N_2F_2, the particular sample for which the measured molecular weight was 68, had as much as 20% of the impurity.

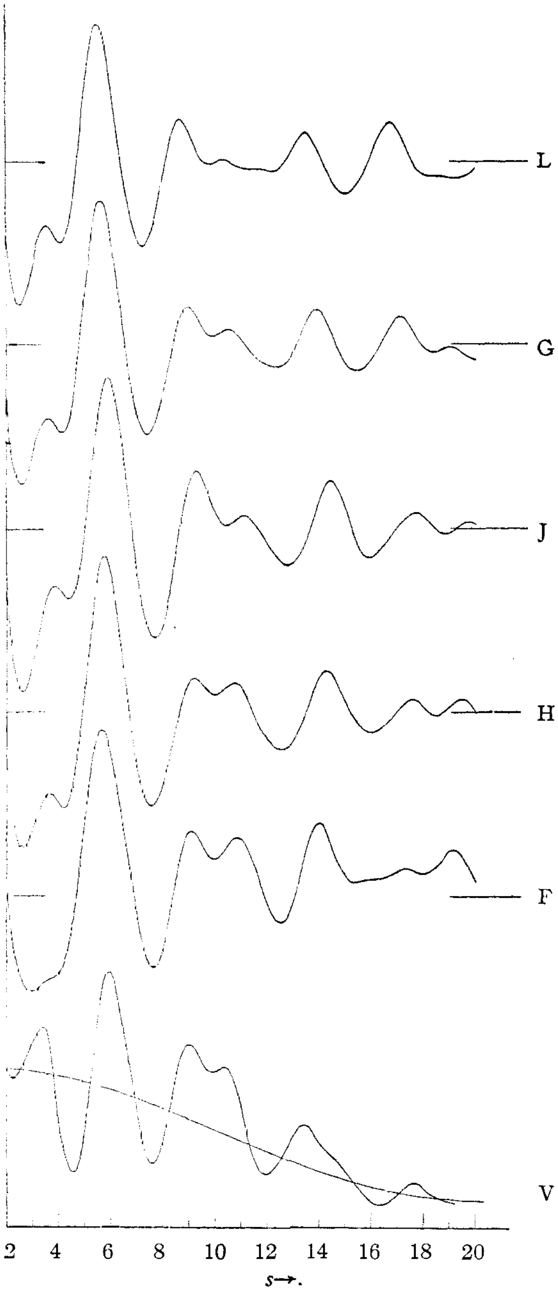


Fig. 1.—Relative intensity curves for N_2F_2.

V: Somewhat idealized sketch of the visual appearance of the photographs.

E:	N=N 1.28 Å.	N—F 1.45 Å.	∠NNF 120° (*cis* + *trans*)
H:	1.28	1.45	116° (*cis* + *trans*)
J:	1.28	1.45	112° (*cis* + *trans*)
G:	1.28	1.50	116° (*cis* + *trans*)
L:	1.28	1.55	116° (*cis* + *trans*)

molecular weight determination was made on the particular sample used. However, since it was prepared parallel to one for which the molecular weight data were obtained, there was thus an indication that some impurity, very likely NF_3, was present.

Analysis of the Photographs

The $s_0 = (4\pi \sin \theta/2)/\lambda$ values computed from visually determined diameters are tabulated (Table I); in the case of the fourth peak, the edges rather than the maximum of density were measured (the value 14.0 is interpolated). It is likely that the tendency to do this resulted in values which are too low for the fourth minimum and too high for the fifth minimum. A radial distribution curve (Walter and Beach method, Fig. 2, R.D.)

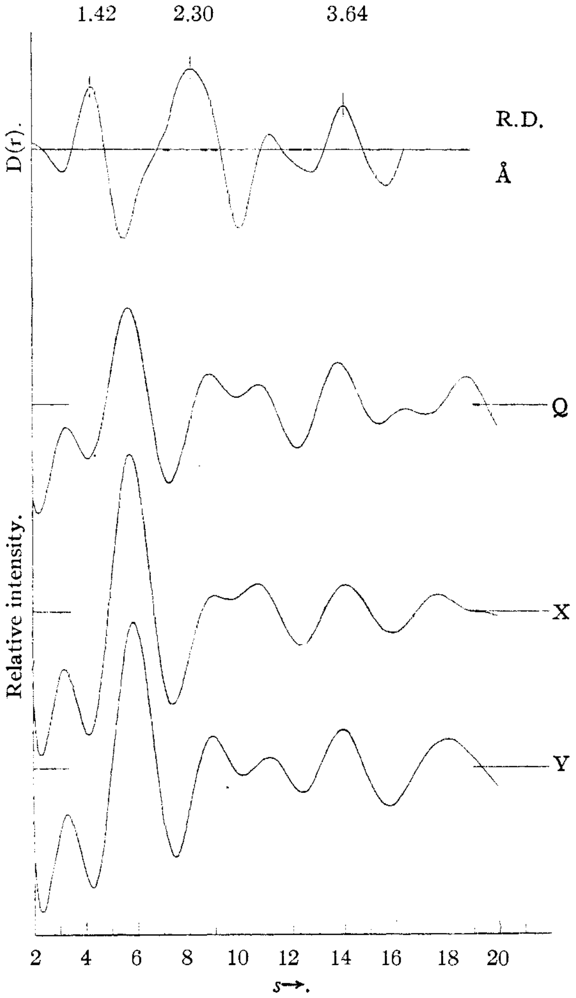
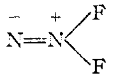
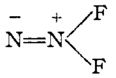


Fig. 2.—R.D. radial distribution curve for N_2F_2. The others are relative intensity curves for

Q: NF_3 (*sym* C_{3v}) N—F 1.45 Å.

X: 
$\overset{-}{N}{=}\overset{+}{N}\begin{smallmatrix}F\\F\end{smallmatrix}$ (planar) 1.45

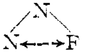
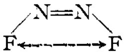
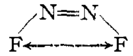
Y: 
$\overset{-}{N}{=}\overset{+}{N}\begin{smallmatrix}F\\F\end{smallmatrix}$ (planar) 1.45

Q: ∠FNF 112°
X: N=N 1.24Å. ∠FNF 122°
Y: N=N 1.16 ∠FNF 116°

Table I

$s_{\text{calcd.}}/s_{\text{obs.}}$

Max.	Min.	s_0	Model J C	Model J T	Model J C + T	Model H C	Model H T	Model H C + T	Model G C	Model G T	Model G C + T	Model F T
1		3.49	(1.006)	(1.180)	(1.109)	(0.925)	(1.129)	(1.074)	(0.914)	(1.103)	(1.020)	(1.146)
	2	4.66	(0.925)	(0.955)	(0.938)	(.895)	(0.944)	(0.901)	(.863)	(0.925)	(0.893)	(0.944)
2		6.07	.977	.960	.965	.949	.949	.949	.926	.926	.924	.970
	3	7.76	.975	1.009	.987	.959	.996	.974	.931	.977	.953	1.027
3		9.21	.994	1.012	1.005	.999	.996	.997	.966	.970	.969	1.023
3a		10.58	1.068	1.040	1.052	.992	1.027	1.014	.974	1.002	.993	1.045
	4	12.21	1.042	1.073	1.050	1.017	1.055	1.028	.988	1.034	1.011	1.069
4a		(13.64)										1.075
(4)		14.0	1.051	1.036	1.029	1.021	1.016	1.018	.987	0.992	0.991	
4b		(14.72)										1.104
	5	16.66	0.954	0.956	0.955	0.968	0.937	0.960	.936	.912	.926	1.074
5		17.83	.976	.998	.993	.984	.979	.984	.966	.959	.958	1.110
Average			1.004	1.010	1.004	.986	.994	.990	.959	.972	.965	1.055
Av. dev.			0.0369	0.0298	0.0306	.0212	.0296	.0237	.0200	.0298	.0255	0.0390
Deduced	N=N:		1.28	1.29	1.28	1.26	1.27	1.27	1.23	1.24	1.24	1.35
	N—F:		1.46	1.46	1.46	1.43	1.44	1.44	1.44	1.46	1.45	1.45
Assumed	∠NNF:		← 112° →			← 116° →			← 116° →			120°

shows prominent atomic spacings at 1.42 Å.—corresponding to N–F distances; 2.30 Å.—corresponding to  distances (the contribution from the *cis*  at 2.50 Å. is not resolved from this peak, but appears as a shoulder); and 3.64 Å.—corresponding to  distances (*trans*).

A large number of theoretical intensity curves were computed for the *cis* and for the *trans* forms of F—N=N—F, in which the ratio of (N—N/N—F) was varied from 0.825 to 0.985, and the ∠NNF from 112 to 125° (Fig. 3). The acceptable models are G, H and J; for the latter the *trans* modification gives the better fit, whereas for the first two, the *cis* form is to be preferred. Models E, L and F may be excluded due to lack of qualitative and quantitative agreement with observation (the first and fifth maxima in E; the third maximum and shoulder in L; the region of the fourth maximum in F). Since we could find no chemical reason why in the preparation either form should predominate, and since the differences between the computed curves, both qualitative and quantitative, are within the limits of discrimination which we believe are justified, equimolar mixtures of the *cis* and *trans* forms are shown in Fig. 1. The qualitative agreement of the various models can best be judged from comparison of these curves, and the quantitative fit from the values in Table I. Insofar as the general form of the pattern is concerned, curve G is most satisfactory; the others do not give as good a fit either with regard to the detailed structure of the third peak or in the region 17 > s > 19.

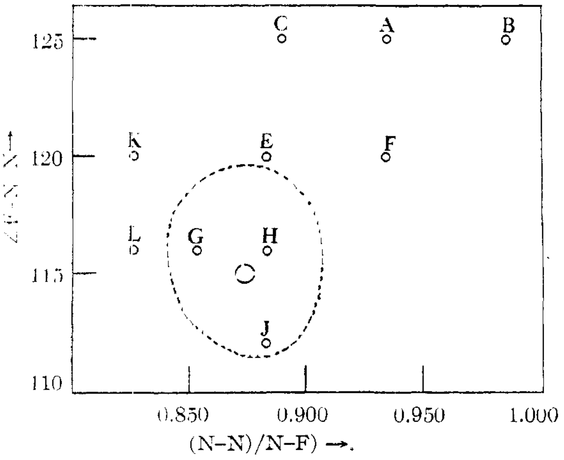


Fig. 3.—The field of parameters covered in the computation of intensity curves for *cis* and *trans* F–N=N–F.

The quantitative agreement between the measured and computed s_0 values is not as good as one would wish. We are thus led to the conclusion that the impurities present did affect the pattern to some extent. To ascertain the disturbances which would be introduced by nitrogen trifluoride, several theoretical intensity curves were computed for that molecule, in which the symmetry C_{3v} and an F–N distance equal to 1.45 Å. were assumed (one of these is curve Q in Fig. 2). Superposition of curves Q and G demonstrates the effect such an impurity would have on the quantitative fit. Unfortunately, due to the fact that only small amounts of N_2F_2 were available (1.5×10^{-3} mole) and that the preparation involved making small quantities of N_3F, which exploded three out of every four runs, we could not retake these photographs nor obtain patterns with more rings. The assigned limits of error are consequently large.

The most probable values deduced (Table I) are

N=N	1.25 ± 0.04 Å.
N—F	1.44 ± 0.04 Å.
∠NNF	115 ± 5°

TABLE II

Bond	Coördination	Molecule	Obs. dist.	Ref.	Dist. predicted[8]
B–F	Trigonal	BF_3	1.30 ± 0.02	9	
	Trigonal	$B(CH_3)_2F$	1.29 ± .02	10	
	Tetrahedral	$(CH_3)_2O:BF_3$	1.43 ± .03	11	1.39[12]
C–F	Tetrahedral	CH_3F	1.396	13	
	Tetrahedral	CF_4	1.36 ± .02	14	
	Tetrahedral	CHF_3	1.34 ± .02	15	1.35
N–F	Pyramidal	NF_3	1.37 ± .02	16	
	∠N=N—F 115°	N_2F_2	1.44 ± .04	This paper	1.37
N–Cl	Pyramidal	$(CH_3)_2NCl$	1.77 ± .02	8	
	Pyramidal	CH_3NCl_2	1.74 ± .02	8	
	∠ONCl 116°	ONCl	1.95 ± .02	8	1.73
N–Br	∠ONBr	ONBr	2.14 ± .02	8	1.86
O–F	∠FOF 105°	OF_2	1.41 ± .05	8	
	∠FON 105°	NO_3F	1.42 ± .05	8	1.41

These check very well with the observed peak positions in the radial distribution curve.

It is interesting to note that although the configuration $\overset{-}{N}{=}\overset{+}{N}\langle{}^{F}_{F}$ is chemically not tenable,[5] it is *almost* satisfactory were one to base his judgment on the intensity curves alone (Figs. 2 and 4). Thus, models X, T and Y give curves which look much like the observed pattern except for details in the region of the third and fifth peaks; the quantitative agreement is not as good as for the F—N=N—F models. Model W is definitely not satisfactory.

Discussion

In azomethane Boersch[6] found for N=N 1.24 ± 0.05 Å.; C-N 1.47 ± 0.06 Å.; and ∠NNC 110 ± 10°. Our final values check this N-N distance and the N-N—X valence angle to well within the experimental errors. The midpoint of the range found satisfactory for the N-F separation is 0.07 Å. larger than that expected for a single bond; the fact that our value checks the one in NF_3 deduced by Bailey, *et al.*,[1] using Badger's rule is of doubtful significance.

In the interatomic distances determined for the fluorides of carbon and for the halides of nitrogen a trend is apparent which is roughly parallel to that reported by Skinner and Sutton[7] in a number of metallic halides. They found that as the number of halide atoms replacing methyl groups attached to the central atom increases, the average metal–halide separation decreases. A point of difference is that whereas the above authors found that the observed metal–halide distances are 2–4% smaller than those computed by means of the Schomaker–Stevenson relation for single bonds,[8] in the case of the carbon fluorides and nitrogen halides, the observed distances are larger than the computed ones, Table II. Indeed, the rather strained postulate proposed for the fluorinated methanes[14] involving a primary ionization followed by double bond resonance, becomes superfluous, and should be replaced by a theory designed to account for the larger than expected C–F bond distance in CH_3F. These observations plus the sizeable number of cases quoted by Schomaker and Stevenson[8] wherein the observed distances are greater than those given by the sum of their radii corrected for electronegativity differences,

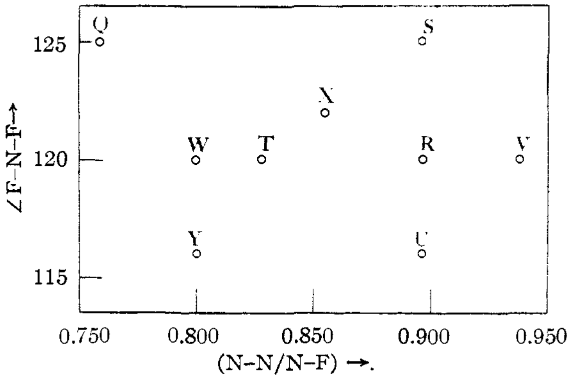


Fig. 4.—The field of parameters covered in the computation of intensity curves for $\overset{-}{N}{=}\overset{+}{N}\langle{}^{F}_{F}$.

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[5] Compounds of the type $\overset{-}{N}{=}\overset{+}{N}\langle{}^{CH_3}_{CH_3}$ have not yet been synthesized; the form $:N{\equiv}N\langle{}^{CH_3}_{CH_3}$ is excluded by the Pauli principle.

[6] H. Boersch, *Monatsh.*, **65**, 311 (1935). This author also reports that in diazomethane the nitrogen atoms are 1.13 ± 0.04 Å. apart, corresponding to a good triple bond.

[7] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944), and previous publications referred to therein.

[8] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[9] H. A. Levy and L. O. Brockway, *ibid.*, **59**, 2084 (1937).

[10] S. H. Bauer and J. M. Hastings, *ibid.*, **64**, 2686 (1942).

[11] S. H. Bauer, G. F. Finlay and A. W. Laubengayer, *ibid.*, **67**, 339 (1945).

[12] S. H. Bauer and J. Y. Beach, *ibid.*, **63**, 1394 (1941).

[13] D. M. Dennison, *Rev. Mod. Phys.*, **12**, 175 (1940).

[14] L. O. Brockway, *J. Phys. Chem.*, **41**, 747 (1937).

[15] J. Scrist, Dissertation, University of Michigan, 1942.

[16] V. Schomaker, private communication.

throws serious doubt on the significance of a number of interpretations of interatomic distances in terms of bond types. It is evident that if interatomic distances are to be used as gages of bond order, tables of radii and methods of computation of separations to be expected for integral bond order must be clearly defined. These discrepancies indicate that this has not been done. I wish to argue that at the present stage of development of valence theory it is dubious whether this can be done.

Our prototype for a single covalent bond is H_2; the lower atomic weight dialkali molecules apparently contain such bonds. The r_e values for the hydrides of the alkali metals and of the halogens might be expected to follow a simple additivity relation were one to allow for the effect of electronegativity differences on the distribution of electrons in the region of the bond. But even there it does not appear possible to set up a completely self consistent scheme, (ref. 8, and Table II) for although the M–H distances in the hydrides of the first row elements are satisfactorily predicted, in SiH_4, PH_3, NaH and HI they are not. It follows that for molecules wherein the basic concept of bond of unit order is in itself fuzzy, wherein the extent of s–p hybridization to form orbitals of maximum stability is expected to change in going from one member of a series to another,[17] one can attach little significance to resonance schemes which purport to account for small deviations of the observed distances from those predicted on the basis of an inconsistent table of radii. The variety of factors which have been listed to date to account for deviations from additivity, such as effects of formal charge, incompleteness of valence shell, electronegativity differences, and the balance between the effect of nuclear charge on one atom as against the increase of electron density on the adjacent one,[7] etc., have in essence been attempts to "save" the notion that a chemical bond in a polyatomic molecule is indeed localized between two atoms. The advantages of such an approach are obvious; it is a good working hypothesis as long as some finer details are overlooked.

Acknowledgment.—The author wishes to express his sincere appreciations to the memory of the late Professor A. W. Browne for his interest in this structure determination and to the Trustee–Faculty Committee on Research of Cornell University for a grant supporting this investigation.

Summary

The diffraction of electrons by the vapor of difluorodiazine led to the following structure for that compound, based on the configuration F—N=N—F (*cis* and *trans*): N—F, 1.44 ± 0.04 Å.; N=N, 1.25 ± 0.04 A.; ∠NNF, 115 ± 5°. An attempt to determine the structure of fluorine azide was not successful.

The discrepancies between the interatomic distances observed and predicted for some fluorine compounds are reviewed, and it is suggested that the use of interatomic distances as a gage of bond orders be limited by discretion.

ITHACA, N. Y. RECEIVED DECEMBER 26, 1946

[17] J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, I, sections 13, 20, 22, and 24 (1935).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE, STATE COLLEGE PENNSYLVANIA]

The Thermodynamics of Butadiene-1,2 from Calorimetric and Spectroscopic Data

BY J. G. ASTON AND G. J. SZASZ[1]

A study of the thermodynamic properties and a comparison of the experimental and calculated potential barriers for butadiene-1,2 (methylallene) and for ethylacetylene (1-butyne) is of interest primarily because they yield additional information about the potential function hindering internal rotation. In our earlier attempt to correlate and predict the magnitude of potential barriers,[2] it was found that a calculation based on hydrogen repulsions only, does not give satisfactory results for compounds containing an excess of electrons (*i.e.*, unsaturated compounds in general, dimethyl ether, dimethyl sulfide, etc.). Before extending the method so that it will yield correct results in such cases, it is desirable to have data on other compounds of this type. The present paper records the experimental data and potential barrier obtained for one of these compounds, butadiene-1,2.

The Calorimeter.—Figure 1 shows a diagram to scale, with explanatory legend of the apparatus used. The calorimeter itself is a modification of the one used by Aston and Eidinoff and is now designated as calorimeter B′. The surrounding system of shields, etc., has been modified to give better control of the temperature of all parts which may affect the calorimeter, and to make faster operation possible. The most important modification is the conical gold-plated copper cover over the glass cap of the resistance thermometer, which is attached to the calorimeter with Wood's metal and around which are wound the leads from the resistance thermometer and constantan heater. This is for the purpose of elimi-

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[1] Phillips Petroleum Fellow, 1945–1947.

[2] Aston, Isserow, Szasz and Kennedy, *J. Chem. Phys.*, **12**, 336 (1944).

[3] Aston and Eidinoff, THIS JOURNAL, **61**, 1533 (1939).