

The Crystal and Molecular Structure of 9-Diazofluorene

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The crystal and molecular structure of 9-diazofluorene has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the monoclinic space group $P2_1$ (C_2^2) with two independent molecules per asymmetric unit. The unit cell, which contains four molecules, has dimensions $a = 16.426$ (5), $b = 5.510$ (2), $c = 11.019$ (3) Å; $\beta = 93.72$ (2)°; $\rho_c = 1.283$, $\rho_x = 1.27$ (2) g cm⁻³. The structure was solved from a combination of Fourier transforms of the weighted reciprocal lattice, translational search of the Patterson function using the minimum function, and Patterson superposition methods. A full-matrix least-squares refinement of the structure by standard methods resulted in an R index of 0.044 for 1804 data for which $F_o^2 > 3\sigma(F_o^2)$. The geometries of the two independent molecules are in excellent agreement. Each molecule is planar and has a linear diazo group. The metric details of the diazo group and the fluorenyl moiety support a polarization model in which substantial negative charge is delocalized throughout the carbocyclic portion of the molecule.

Introduction

In the course of our investigations into the structural and reaction chemistry of transition-metal complexes which contain a ligating $-N_2$ diazo group (Cowie, Haymore & Ibers, 1976) we have recently determined the crystal and molecular structure of a nickel–9-diazofluorene complex (Nakamura, Yoshida, Cowie, Otsuka & Ibers, 1977; Otsuka, Nakamura, Koyama & Tatsuno, 1975). The mode of coordination involves both N atoms. In order to ascertain the geometrical consequences on the ligand of ligation it is necessary to know the structural details of the uncoordinated diazo compound. With this in mind, we undertook the reinvestigation of structure of 9-diazofluorene (I) which is a relatively stable, highly crystalline compound.

Our original interest in (I) arose in connection with a prediction of its crystal packing based upon ESR measurements (Brandon, Closs, Davoust, Hutchison, Kohler & Silbey, 1965). Although a preliminary report of our original study was presented (Corfield, Hamilton, Ibers, Koenig & La Placa, 1967) the complete results were never fully reported. In the intervening period, a determination of the structural details of 2-bromo-9-diazofluorene has appeared (Griffiths & Hine,

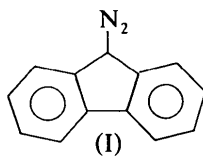
1970a). However, the quality of derived parameters is rather poor. Very few compounds containing the diazo group have been structurally characterized. Yet the chemistry of the diazo functionality remains of considerable interest (Duerr & Schmidt, 1974) and much of the chemistry centers on 9-diazofluorene in preference to other simpler compounds, *e.g.* diazomethane, whose instability does not allow close examination. For these reasons, we report here the results of the redetermination of the structure of 9-diazofluorene.

Experimental

Crystal preparation and determination of crystallographic data

9-Diazofluorene was prepared from the corresponding hydrazone by the mercuric oxide method (Schönberg, Awad & Latif, 1951). An analytically pure sample was dissolved in a minimum of boiling diethyl ether and the saturated solution was allowed to stand at 0°C. Long red-orange needles were obtained when the solvent had evaporated. A crystal was chosen and fractured normal to its needle axis to yield a fragment of appropriate size for X-ray examination. This crystal fragment was then sealed inside an Ar-filled glass capillary.

Preliminary Weissenberg and precession photographs are in agreement with previous results (Corfield *et al.*, 1967) and indicate that the crystal belongs to the monoclinic system. Systematic extinctions are $0k0$ ($k = 2n + 1$), indicative of space groups $P2_1/m$ (C_{2h}^2) (centrosymmetric) or $P2_1$ (C_2^2) (non-centrosymmetric). Previous results had shown



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that there are two independent molecules in the asymmetric unit of the non-centrosymmetric space group $P2_1$. Accurate cell parameters were obtained from a least-squares refinement of the setting angles of 14 reflections that had been hand-centered on a Picker FACS-I diffractometer (Doedens & Ibers, 1967). These reflections were chosen from diverse regions of reciprocal space [$41.2^\circ \leq 2\theta(\text{Cu } K\alpha_1) \leq 48.2^\circ$] and were obtained using a narrow source. Cell dimensions and other pertinent data are shown in Table 1.

Data were collected on a Picker four-circle computer-controlled diffractometer in shells of 2θ with the θ - 2θ scan technique. Background counts were measured at both ends of the scan range with the counter and crystal stationary. If the observed peak intensity was less than 3σ , as defined by the background counting statistics, the reflection was rescanned and each background recounted for twice its original time. The results of the two scans and two back-

grounds were then combined. The intensities of six standard reflections were measured every 100 reflections for $2\theta \leq 125^\circ$. For higher values of 2θ , three reflections were measured. The fluctuations observed in these standards were within the range of counting statistics; hence the crystal maintained its chemical integrity throughout data collection.

The intensities of 2754 reflections with $5^\circ \leq 2\theta \leq 160^\circ$ were measured with Ni filtered Cu $K\alpha$ X-radiation. All members of the form $\{hkl\}$ were measured for $2\theta \leq 50^\circ$; only reflections of the type $\pm h, -k, +l$ were measured at higher angles. Data were processed in the usual way, with a value of 0.04 used for p in the calculation of $\sigma(F_o^2)$. Of the observed reflections, 2203 are unique and of these 1804 have $F_o^2 > 3\sigma(F_o^2)$. A correction for absorption was applied to the data using Gaussian integration.

Table 1. Summary of crystal data, intensity collection, and refinement

Compound	Diazofluorene
Formula	$\text{C}_{13}\text{H}_8\text{N}_2$
a	16.426 (5) Å
b	5.510 (2)
c	11.019 (3)
β	$93.72 (2)^\circ$
V	995.2 \AA^3
Z	4
Formula weight	192.22
Density	1.283 g cm^{-3} (calc.) 1.27 (2) g cm^{-3} (exp.)
Space group	$P2_1 (C_2^2)$
Crystal dimensions	$0.55 \times 0.45 \times 0.25 \text{ mm}$
Crystal shape	Hexagonal needle with well-developed faces of the forms $\{100\}$, $\{101\}$, $\{10\bar{1}\}$
Crystal volume	0.0273 mm^3
Temperature	24°C
Radiation	Cu $K\alpha_1$ ($\lambda = 1.540562 \text{ \AA}$) prefiltered with 1 milli-inch of Ni foil
μ	5.75 cm^{-1}
Transmission factors	0.809–0.905
Receiving aperture	$7.0 \times 4.0 \text{ mm}$; 30 cm from crystal
Take-off angle	4.0°
Scan rate	$2.0^\circ \text{ min}^{-1}$ in 2θ
Scan range	0.9° below $K\alpha_1$ to 0.9° above $K\alpha_2$
Background counts	10 s for $2\theta \leq 125^\circ$ 20 s for $2\theta > 125^\circ$
2θ limits	5 – 160°
Final number of variables	270
Unique data used including $F_o^2 \leq 0$	2203
Unique data with $F_o^2 > 3\sigma(F_o^2)$	1804
R (on F^2)	0.080
R_w	0.112
R [on F , $F_o^2 > 3\sigma(F_o^2)$]	0.044
R_w	0.057
Error in observation of unit weight	1.69e^2

Determination of the structure

The structure was determined and refined initially with an earlier set of data.* Probable orientations for each of the two independent molecules in the cell could be found by inspection of the weighted reciprocal lattice, if the long axes of the molecules were assumed to be approximately perpendicular to b . The origin peaks of the Fourier transforms of these large planar molecules are expected to be seen as prominent, rod-shaped regions in reciprocal space, radiating from the origin (Bolton, 1963). Parts of the weighted reciprocal lattice showing these rods are reproduced in Fig. 1. Inspection of a sharpened Patterson function confirmed these orientations, as there were many peaks in sheets perpendicular to the rods found in the reciprocal lattice.

Idealized coordinates for all atoms in an individual

* This data set was collected by S. J. La Placa at Brookhaven National Laboratory.

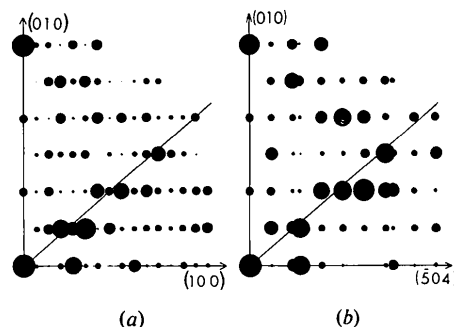


Fig. 1. Portions of the weighted reciprocal lattice. The diameters of the circles are proportional to the magnitudes of the normalized structure factors, E . (a) Part of the $hk0$ layer, showing the origin peak of the transform for molecule 1. (b) Reflections near the $5h,k,4l$ layer, showing the origin peak of the transform for molecule 2.

molecule were calculated on a Cartesian set of axes, with planarity of the molecule assumed. All possible intramolecular vectors for a molecule in one of the possible orientations (molecule 1 in the final structure) were found to be consistent with peaks in the Patterson map. The location of this molecule in the unit cell was found by a translational search using the minimum function (Nordman, 1966). A 30-fold superposition of the Patterson function was calculated using the minimum function, based on the coordinates of molecule 1 and the molecule related to it by the screw axis. While this map did in fact contain adequate information to enable us to locate the second molecule in the asymmetric unit, it appeared featureless on a preliminary inspection. A successful attempt to improve the resolution was made by obtaining the Fourier transform of positive regions of the minimum function (Simonov, 1961; Corfield & Rosenstein, 1966). Phases from the Fourier transform were applied to the observed structure factors, and an ordinary Fourier synthesis then clearly revealed the position of the second molecule.

Refinement of the structure

The structural refinement was carried out with full-matrix, least-squares techniques and the new data set. The function minimized initially was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weights, w , are taken to be $4F_o^2/\sigma^2(F_o^2)$. Here, only the 1804 unique data having $F_o^2 > 3\sigma(F_o^2)$ were used. Atomic scattering factors for the nonhydrogen atoms were taken from the tabulation of Cromer & Waber (1974). H scattering factors used were those of Stewart, Davidson & Simpson (1965). Since $P2_1$ is a polar space group it is necessary, in principle, to fix the sense of the polar axis in the crystal of choice through inclusion of anomalous dispersion terms and comparison of reflections no longer equivalent because of the failure of Friedel's law. However, through sample calculations we established that the effects of anomalous dispersion are too small to be discernible experimentally in the present structure, containing, as it does, only the very light scatterers N, C, and H. Consequently, errors in the structure determination arising from neglect of anomalous scattering are negligible. Isotropic refinement of the nonhydrogen atoms resulted in agreement indices of $R = 0.119$ and $R_w = 0.158$. These indices on F_o are defined as follows: $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2}$. After two cycles of anisotropic refinement, the agreement indices had decreased to 0.072 and 0.096. The positions of the 16 H atoms were then calculated assuming trigonal geometry of the aromatic C atoms and using a C—H distance of 0.95 Å. Each H atom was assigned a thermal parameter 1.0 Å² greater than the equivalent isotropic thermal parameter of the

Table 2. Positional parameters of the nonhydrogen atoms of 9-diazo fluorene

Estimated standard deviations in the least significant figures are given in parentheses in this and all subsequent tables.

	x	y	z
C(14a)	-0.11004 (15)	0.33344 (84)	-0.49565 (28)
C(14)	-0.08142 (17)	0.49811 (94)	-0.57928 (34)
C(13)	-0.10078 (20)	0.46531 (99)	-0.69984 (35)
C(12)	-0.14915 (20)	0.2703 (10)	-0.74148 (30)
C(11)	-0.17741 (17)	0.10408 (91)	-0.66100 (29)
C(19a)	-0.15831 (15)	0.13387 (83)	-0.53851 (25)
C(19)	-0.17864 (16)	0	-0.43211 (26)
C(18a)	-0.14331 (16)	0.11508 (88)	-0.32377 (26)
C(18)	-0.14462 (20)	0.05872 (98)	-0.20235 (31)
C(17)	-0.10336 (25)	0.2097 (12)	-0.11916 (34)
C(16)	-0.06101 (24)	0.4119 (11)	-0.15809 (41)
C(15)	-0.05936 (19)	0.4678 (10)	-0.27841 (37)
C(14b)	-0.10057 (16)	0.31993 (92)	-0.36349 (28)
N(11)	-0.22868 (15)	-0.18892 (82)	-0.43340 (23)
N(12)	-0.27148 (18)	-0.34817 (85)	-0.43436 (29)
C(24a)	0.41719 (16)	0.33564 (87)	0.10593 (23)
C(24)	0.39534 (18)	0.49776 (85)	0.01288 (26)
C(23)	0.32450 (21)	0.46167 (98)	-0.05736 (28)
C(22)	0.27477 (20)	0.26258 (99)	-0.03585 (31)
C(21)	0.29458 (18)	0.09903 (91)	0.05640 (28)
C(29a)	0.36672 (16)	0.13609 (83)	0.12753 (24)
C(29)	0.40527 (17)	0.00716 (82)	0.22922 (25)
C(28a)	0.48051 (16)	0.12745 (83)	0.27069 (23)
C(28)	0.53942 (18)	0.07982 (90)	0.36339 (26)
C(27)	0.60596 (20)	0.2326 (10)	0.37695 (29)
C(26)	0.61407 (19)	0.42974 (96)	0.30068 (31)
C(25)	0.55503 (19)	0.48083 (90)	0.20903 (28)
C(24b)	0.48733 (16)	0.32898 (86)	0.19364 (22)
N(21)	0.37536 (15)	-0.18871 (80)	0.27930 (22)
N(22)	0.34938 (17)	-0.35499 (83)	0.32208 (26)

C atom to which it is attached. The contribution of the H atoms to the total scattering was fixed in subsequent refinement cycles. In the final two cycles all 2203 unique F_o^2 values (including those for which $F_o^2 < 0$) were employed in the minimization of the function $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Agreement indices on F_o^2 are defined as $R = \Sigma |F_o^2 - F_c^2| / \Sigma F_o^2$ and $R_w = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$. Final agreement indices, based on 2203 unique F_o^2 values and 270 variables, are $R = 0.080$ and $R_w = 0.112$. The conventional index on $|F_o|$, for the 1804 reflections having $F_o^2 > 3\sigma(F_o^2)$, is 0.044. An analysis of $\Sigma w(F_o^2 - F_c^2)^2$ as a function of F_o^2 , setting angles, and Miller indices shows no unusual trends. The standard deviation of an observation of unit weight is 1.69 e². A final difference Fourier synthesis is essentially featureless with the highest peak and deepest trough equal to 0.13 and -0.21 e Å⁻³, respectively.

The final positional parameters of the nonhydrogen atoms appear in Table 2.*

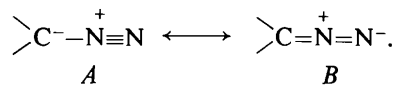
* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33197 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

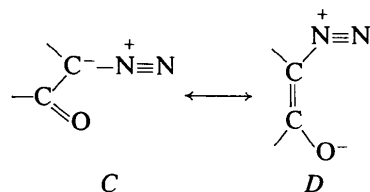
The crystal structure of 9-diazofluorene consists of two pairs of independent molecules per unit cell. Fig. 2 contains a stereoscopic representation of the cell. The molecules stack so that the polar diazo groups form a channel through the cell along *y*. The channel consists of a zigzag chain of N₂ groups which may result from an electrostatic attraction between atoms N(1) and N(2) on adjacent molecules. The intermolecular N(1)–N(2) contacts average 3.071 (5) Å, slightly longer than twice the van der Waals radius of N, 3.0 Å (Pauling, 1960). The shortest intermolecular contact, 2.56 Å, occurs between H atoms bound to atoms C(1) and C(2). Neither this nor any other intermolecular contact is unexpectedly short. A representation of the molecule is shown in Fig. 3, which also contains the labeling scheme used.

The bonding parameters for the two unique molecules are listed in Table 3. Note that the metrical details of the two independent molecules are in excellent agreement and therefore this discussion will be limited primarily to average parameters obtained over both molecules (see Table 4). The compound 9-diazofluorene is highly planar as judged by an average deviation of atoms from the carbocyclic least-squares plane of 0.008 Å. This is in accord with intuition and observation of other structurally characterized fluorenyl compounds (Burns & Iball, 1955; Dorset, Hybl & Ammon, 1972; Griffiths & Hine, 1970*a,b*; Luss & Smith, 1972; Silverman, Krukonić & Yannoni, 1967, 1968, 1973). The N atoms of the diazo group deviate slightly [0.02 and 0.06 Å for atoms N(1) and N(2) respectively] from the least-squares plane through the molecule. This is not surprising since the N atoms comprise the only noncyclic portion of the molecule and thus possess higher degrees of vibrational freedom.

However, this deviation may also be indicative of the electronic structure of the diazo functionality. Structures *A* and *B* are important canonical forms of any diazo compound:



A has been shown to be the major contributor and becomes especially predominant in those cases where the negative charge centered on the C atom to which the diazo group is bound can be attenuated by delocalization. An example of this is the markedly enhanced stability of α -keto diazo compounds compared with that of nonconjugated diazoalkanes (Zollinger, 1961). The additional stability arises from form *D*, which becomes the major contributor:



Form *A* should also predominate in (I) where the degree of conjugation is high. Thus the C(9)–N(1) bond may involve little π interaction. Conjugation between the N₂ and the carbocyclic system is relatively unimportant and the N atoms are not as constrained to the plane of the fluorenyl fragment as they would be in a system of more extensive conjugation.

The individual bonding parameters of the diazo group in (I) are also strongly indicative of the importance of form *A*. The N(1)–N(2) bond length is 1.126 (4) Å (Table 3), only slightly longer than the

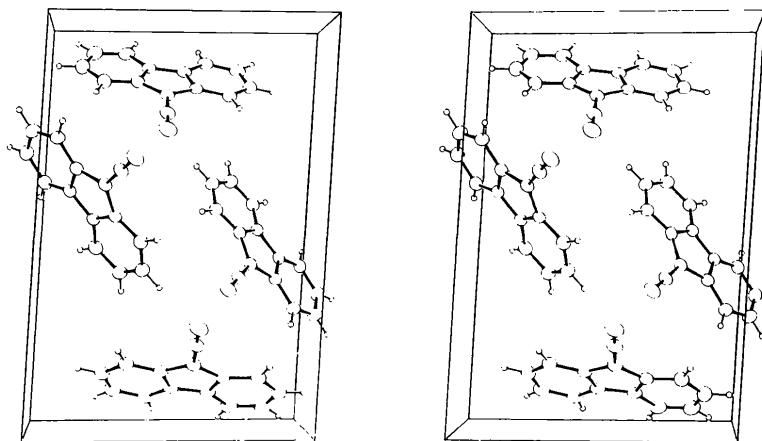


Fig. 2. Stereoscopic view of a unit cell of 9-diazofluorene. The *x* axis is vertical from top to bottom, the *y* axis is perpendicular to the paper going away from the reader, and the *z* axis is horizontal to the right. The vibrational ellipsoids of nonhydrogen atoms are drawn at the 20% level. Hydrogen atoms have been drawn arbitrarily small.

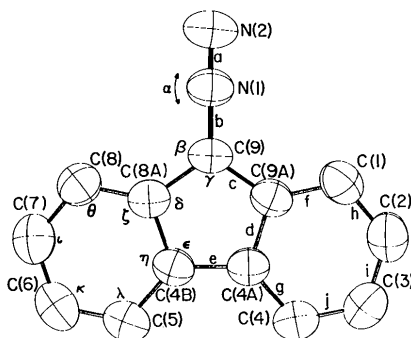


Fig. 3. A perspective representation of one of the independent molecules of 9-diazofluorene. The vibrational ellipsoids are drawn at the 50% probability level. The labeling schemes are also shown.

N—N triple-bond distance, 1.097–1.098 Å, as observed in dinitrogen and aromatic diazonium compounds (Wilkinson, 1957; Rømming & Tjørnholm, 1968), and much shorter than the bond lengths observed for N—N double bonds, e.g. 1.243 (3) Å in *trans*-azobenzene (Brown, 1966). This short distance is expected if *A* is the major contributing form and is the rule in all other structurally characterized diazo compounds (Abraham, Cochran & Rosenstein, 1971; Ansell, 1969; Cox, Thomas & Sheridan, 1958; Griffiths & Hine, 1970a; Hope & Black, 1972; Presley & Sass, 1970).

Table 3. Distances (Å) and angles (°) in the two independent molecules of 9-diazofluorene

See Fig. 3 for notation of distances and angles. A number of angles, e.g. C(8)—C(8a)—C(9), are not included here. In view of the essential planarity of the molecules these angles may be directly and reliably derived from those given. For example: $\angle C(8)–C(8a)–C(9) = [360.0 - (\delta + \zeta)]^\circ$.

Distance or angle	Molecule 1	Molecule 2
<i>a</i>	1.124 (4)	1.127 (4)
<i>b</i>	1.326 (4)	1.321 (4)
<i>c</i>	1.442 (4), 1.440 (4)	1.439 (4), 1.450 (4)
<i>d</i>	1.419 (4), 1.414 (5)	1.407 (4), 1.407 (4)
<i>e</i>	1.456 (4)	1.456 (4)
<i>f</i>	1.376 (4), 1.375 (4)	1.393 (4), 1.386 (4)
<i>g</i>	1.396 (5), 1.385 (5)	1.389 (4), 1.393 (4)
<i>h</i>	1.376 (5), 1.382 (6)	1.381 (5), 1.380 (5)
<i>i</i>	1.396 (6), 1.396 (7)	1.397 (5), 1.385 (5)
<i>j</i>	1.358 (5), 1.363 (6)	1.370 (5), 1.383 (5)
α	179.6 (3)	179.5 (3)
β	124.8 (3), 124.7 (3)	124.9 (3), 125.0 (3)
γ	110.3 (3)	110.1 (3)
δ	106.2 (2), 106.0 (3)	106.5 (2), 105.7 (2)
ϵ	108.3 (3), 109.1 (3)	108.5 (3), 109.3 (3)
ζ	120.4 (3), 121.4 (3)	120.6 (3), 121.0 (3)
η	119.3 (3), 119.4 (3)	120.0 (3), 119.7 (3)
θ	119.2 (3), 118.1 (4)	118.0 (3), 118.3 (3)
<i>ι</i>	120.6 (3), 120.6 (4)	121.6 (3), 121.3 (3)
κ	121.1 (3), 121.4 (4)	120.2 (3), 120.8 (3)
λ	119.5 (3), 119.1 (4)	119.5 (3), 118.9 (3)

Table 4. Distances (Å) and angles (°) in 9-diazofluorene (I), 9-fluorenone (II) and the fluorenyl anion (III)

	(II)†	(I)*	(III)‡
<i>a</i>		1.126 (4)§	
<i>b</i>		1.324 (4)	
<i>c</i>	1.486 (5)	1.443 (5)	1.413 (9)
<i>d</i>	1.390 (5)	1.412 (5)	1.425 (5)
<i>e</i>	1.475 (5)	1.456 (4)	1.433 (10)
<i>f</i>	1.379 (5)	1.383 (4)	1.418 (3)
<i>g</i>	1.380 (5)	1.391 (5)	1.400 (10)
<i>h</i>	1.385 (5)	1.380 (6)	1.353 (8)
<i>i</i>	1.376 (5)	1.393 (6)	1.391 (5)
<i>j</i>	1.389 (5)	1.369 (5)	1.378 (6)
α		179.6 (3)	
β		124.8 (3)	
γ	105.8 (3)	110.2 (3)	108.4 (3)
δ	108.4 (3)	106.1 (3)	108.2 (3)
ϵ	108.8 (3)	108.8 (3)	107.7 (3)
ζ		120.8 (3)	
η		119.6 (3)	
θ		118.4 (4)	
<i>ι</i>		121.1 (4)	
κ		120.8 (4)	
λ		119.3 (4)	

* This work.

† Luss & Smith (1972).

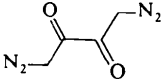
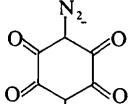
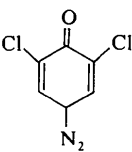
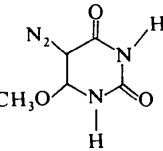
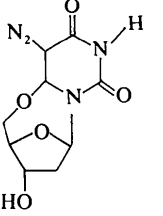
‡ Zerger *et al.* (1974).

§ These values are the weighted averages for the two independent molecules. The number in parentheses is the standard deviation of a single observation. It is the larger of that estimated from the inverse matrix or that from the averaging process.

Table 5 is a compilation of the metrical details of the diazo groups in these compounds. The CNN angle is in all cases very nearly linear [179.6 (3)° in (I)]. The structural feature of (I) which least approximates expectations based upon form *A* is the C(9)—N(1) bond length, 1.324 (4) Å. This is considerably shorter than the C(*sp*²)—N single-bond distances observed in *trans*-azobenzene and the benzenediazonium cation, 1.433 (3) and 1.425 (5) Å respectively (Brown, 1966; Rømming & Tjørnholm, 1968). This short bond length is not an isolated phenomenon, however, as all other diazo compounds listed in Table 4 exhibit similar bond lengths. These lengths are much more akin to those of the C(*sp*²)—N partial double bonds of pyridine and formamide, 1.340 (1) and 1.343 (7) Å respectively (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958; Kurland & White, 1957). This double-bond character suggests a non-negligible contribution from form *B*. A molecular orbital treatment of the diazo system might lead to better understanding of this apparent dichotomy than is possible with naïve resonance models such as *A* and *B*.

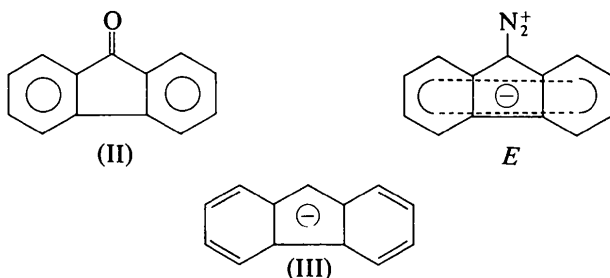
The metrical details of the fluorenyl fragment of 9-diazofluorene are, however, consistent with a predominant contribution from form *A*. Parry & Warren (1965)

Table 5. Distances (Å) and angles (°) in diazo compounds

Compound	C-N	N-N	∠C-N-N	Reference
	1.313 (2)	1.114 (2)	176.8 (1)	1
	1.351 (10)	1.107 (10)	177.9 (9)	2
	1.37 (2)	1.10 (2)	178.8 (1)	3
	1.332 (7)	1.113 (7)		4
	1.308 (7)	1.120 (7)		4
H ₂ CN ₂	1.32	1.12		5
(I)	1.324 (4)	1.126 (4)	179.6 (3)	6

References: (1) Hope & Black (1972). (2) Ansell (1969). (3) Presley & Sass (1970). (4) Abraham *et al.* (1971). (5) Cox *et al.* (1958). (6) This work.

have shown that the reactivity of (I) is much more characteristic of an aromatic system than is that of 9-fluorenone, (II). This aromaticity arises from form *E*, in which the negative charge generated at atom C(9) by complete polarization of the diazo group has been delocalized throughout the π system of the entire C₁₃ moiety.



Thus, the planar π system involves 14 electrons, which satisfies Hückel's $4n + 2$ criterion for aromaticity. Similar delocalization of the positive charge resulting from the polarization of the keto group in (II) yields a system which is distinctly antiaromatic, as it involves $4n$ π electrons ($n = 3$). The structural details of 9-diazofluorene and 9-fluorenone also reflect a difference in aromatic character. Table 4 contains a comparison of the pertinent structural parameters of (I) and (II) (Luss & Smith, 1972). Also included are values for the highly aromatic fluorenyl anion (III) as derived by Stucky and co-workers from the structural determinations of two ion-pair complexes (Brooks, Rhine & Stucky, 1972; Zerger, Rhine & Stucky, 1974). Predictably, the major differences arise within the sets of parameters of the five-membered ring, where the effects of aromaticity are most evident. The three bond lengths in question, *c*, *d* and *e*, all exhibit a trend in which the values for 9-diazofluorene are between those of the ketone and the carbanion, approximating the values of the latter more closely. Bond length *c* in (I), 1.443 (5) Å, is much shorter than that of (II), 1.486 (5) Å, though considerably longer than the value of 1.413 (9) Å observed for (III). This difference is consistent with the enhanced interaction of atom C(9) with the benzenoid fragments in (I) and (III) relative to (II). Bond length *d* for the ketone, 1.390 (5) Å, approximates those of the remaining benzenoid parameters, *f*-*j*. Thus each six-membered ring is only slightly perturbed by the rest of the molecule. However, for diazofluorene and the anion the values of bond length *d* are significantly longer than those of the benzenoid periphery, which implies that substantial π interactions throughout each molecule are present. Further corroboration of a sequestering of the benzene rings in ketone (II), not present in (I) or (III), arises from the differences in bond length *e*. The longer distance in the fluorenone molecule indicates that the two benzene rings interact to a much smaller extent than they do in compounds (I) and (III), for which *e* is significantly shorter. The remaining bond lengths exhibit less pronounced variances but generally follow the trend mentioned above. Thus, the bond-length data are totally consistent with the partial aromaticity of 9-diazofluorene. This aromaticity is predicted by the polarization model for the diazo group presented above.

The bond angles in 9-diazofluorene exhibit no unusual features. A decrease from 120° is observed for angles θ and κ . A similar deviation is present in other fluorenyl structures and generally occurs in compounds in which a benzo ring is fused to a five-membered ring (Bordner, Stanford & Dickerson, 1970; Kalyani, Manohar & Mani, 1967; Kalyani & Vijayan, 1969; Smith & Barrett, 1969). The variances seen for angles γ , δ , and ϵ , between compounds (I), (II) and (III), are manifestations of the bond-length changes. For example, a comparison of parameters for diazofluorene and

fluorenone reveals that as c is shortened from 1.486 (5) Å, in (II) and (I) respectively, angles γ and δ are constrained to vary by the magnitudes observed.

Programs used

The Northwestern absorption program, *AGNOST*, includes the Coppens–Leiserowitz–Rabinovich logic for Gaussian integration and the Tompa analytical method. In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's *FORDAP* Fourier summation program, Johnson's *ORTEP* thermal ellipsoid plotting program, and Busing's and Levy's *ORFFE* error function program. Our full-matrix, least-squares program, *NUCLS*, in its non-group form closely resembles the Busing–Levy *ORFLS* program. Final calculations were performed by remote telephone hook-up to the CDC 7600 computer at Lawrence Berkeley Laboratory. The same programs were used. The diffractometer was run under the disk-oriented Vanderbilt system (Lenhert, 1975).

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