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Molecular structure of 6-(*N*,*N*-dimethylamino)fulvene from a joint gas-phase electron diffraction and quantum-chemical study

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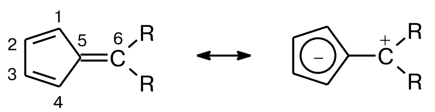
The molecular structure of 6-(*N*,*N*-dimethylamino)fulvene was studied by gas-phase electron diffraction and quantum-chemical methods (HF/6-31G(d), MP2/3Z, MP2/4Z, density functional theory with the B3LYP/6-31G(d) and PBE/3Z functionals). Pronounced flattening of the nitrogen atom and equalization of the intracyclic C—C bonds were found to be a consequence of the electron delocalization in the molecule.

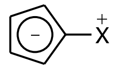
Key words: gas-phase electron diffraction, *ab initio* quantum-chemical calculations, quantum-chemical calculations, density functional theory, fulvenes, 6-(*N*,*N*-dimethylamino)fulvene, molecular structure.

Fulvenes **1**, the derivatives of cyclopentadiene with the exocyclic C=C bond, significantly differ from the cyclic and open-chain polyenes in their physicochemical characteristics and reactivity.[1] Large molecular dipole moments (1.1 D for fulvene[2] and 1.94 D for 6,6-dimethylfulvene[3]), specific features of the electronic spectra, and the ability to add organolithium and organomagnesium compounds at the exocyclic double bond to give the salts of substituted cyclopentadienide anions unambiguously point to partiial delocalization of two π-electrons of the C(5)=C(6) double bond over the five-membered ring. In terms of the resonance structures this situation is usually described as a substantial contribution of the bipolar structure **1B**.



1A **1B**

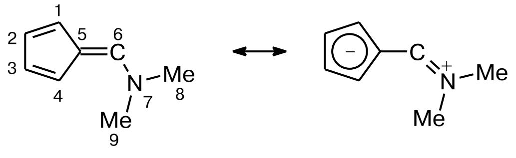
In the limiting case such a delocalization is observed in the heteroatomic bipolar cyclopentadienylides **2** and manifests itself not only in an increase in the molecular dipole moments (6.1 D for **2c** and 7.11 D for **2d**) but also in pronounced regular equalization of the carbon—carbon bond lengths.[4—7]



2a—e

X = N≡N (**a**), NMe$_3$ (**b**), SMe$_2$ (**c**), PPh$_3$ (**d**), NC$_5$H$_5$ (**e**)

6-(*N*,*N*-Dimethylamino)fulvene **3** is intermediate between the unsubstituted fulvene **1** (R = H) and cyclopentadienylides **2**. In molecule **3** the lone electron pair of the N atom is involved in the conjugated system and to a great extent delocalized. The dipole moment of molecule **3** is 5.07 D. The barrier to rotation about the C(6)—N(7) bond is increased to 12 kcal mol^{-1} and strongly depends on the solvent polarity.[8]



3

Obtaining structural data on fulvenes in the gas phase (in the absence of the crystal lattice effects) is of considerable theoretical interest. Earlier, such data were obtained[9] for the unstable unsubstituted fulvene by microwave spectroscopy. In this work we carried out a gas-phase electron diffraction study of 6-(*N*,*N*-dimethylamino)fulvene (**3**) and performed the *ab initio* and density functional quan-

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tum-chemical calculations of the molecular structure of this compound.

Experimental

The sample of compound **3** was synthesized following a known procedure.[10] The electron diffraction patterns were obtained on an EG-100M electron diffraction apparatus with an accelerating voltage of 50 kV and two nozzle—plate distances, 375 mm (three plates) and 169 mm (two plates). The nozzle temperature was 70 °C. The scattered electron beam wavelength was determined using the electron diffraction patterns of benzene obtained simultaneously with those of **3**. Photometric measurements of the electron diffraction patterns were performed on an MFS-12000CX scanner calibrated against the photometric wedge. An original procedure[11,12] for primary processing of experimental information was employed, which included search for the center of the diffraction pattern and conversion of the two-dimensional scattering intensity, $I(x,y)$, into the one-dimensional scattering intensity, $I(s)$. The experimental scattering intensity curves (Fig. 1) were modified by dividing by the opening angle of the sector and the atomic scattering intensity. The background lines in the intensity curves were spline approximated. In calculating the radial distribution curve the experimental molecular scattering intensity was complemented by a theoretical model on the left until zero and on the right until damping (50 Å^{-1}) and divided by the g-function of the term with the maximum contribution (C—C term).

Quantum-chemical calculations were carried out using the PRIRODA program package[13,14] on an MBC 1000M computer cluster at the Interdepartmental Supercomputer Center (Moscow, Russian Federation).

Structural Analysis

Low symmetry of molecule **3** precludes determination of all independent geometric parameters using the gas-phase electron diffraction technique. Because of this the model and the initial approximation were to a great extent chosen based on the results of high-level quantum-chemical calculations. This approach has proved itself to be efficient and justified.[15]

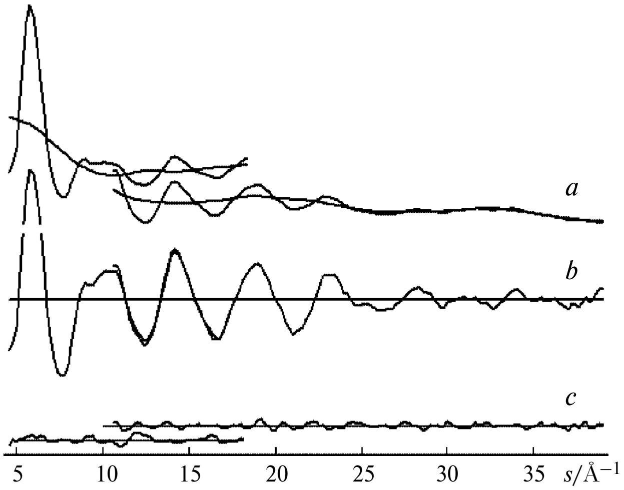

Fig. 1. The experimental scattering intensitiy curves $I(s)$, the background lines (*a*), molecular scattering intensitiy (*b*), and the difference curves (*c*) for 6-(*N*,*N*-dimethylamino)fulvene (**3**) (s is the scattering parameter).

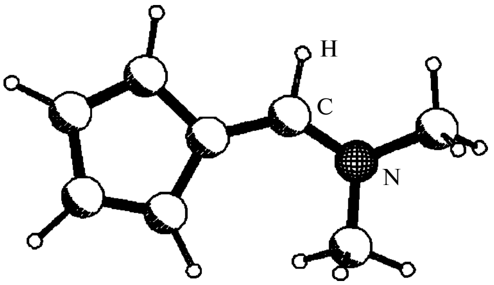

Fig. 2. Molecular structure of 6-(*N*,*N*-dimethylamino)fulvene (**3**) obtained from MP2/4Z calculations.

The molecular structure of **3** obtained from the most rigorous MP2/4Z calculations is shown in Fig. 2. The main geometric parameters calculated by different computational methods are listed in Table 1.

The results obtained using all the methods employed are in good agreement with one another. According to calculations (see Table 1, the B3LYP/6-31G(d), PBE/3Z, MP2/3Z, and MP2/4Z methods), the formally double bonds C(1)=C(2) and C(3)=C(4) and the exocyclic bond C(5)=C(6) are appreciably lengthened compared to the standard value (1.34 Å), whereas the formally ordinary bonds C(1)—C(5), C(4)—C(5), and C(2)—C(3) are shorter than the corresponding reference bond length (1.533 Å). The atoms of the conjugated system can be treated as lying in virtually the same plane (the N atom deviates from the plane by 0.11 Å). The dimethylamino group is also appreciably flattened, namely, the N atom deviates from the plane passing through the C(6), C(7), and C(8) atoms only by 0.08 Å. The pyramidality, d, of the nitrogen atom ($d = 360° - (\angle C(6)—N(7)—C(8) + \angle C(6)N(7)C(9) + \angle C(8)N(7)C(9))$ is only 1° (*cf.* zero for the planar bond system and 27.3° for trimethylamine[16]). According to calculations, an increase in the pyramidality of the dimethylamino group causes a substantial increase in the internal energy of molecule **3**. The gas-phase electron diffraction reliability factor, Rf, changes in a similar way (Fig. 3).

To perform structural analysis, the geometric parameters were divided into six groups to reduce the cross correlations. For three groups of parameters including the internuclear distances (relatively long valence bonds C(1)—C(5), C(4)—C(5), C(2)—C(3), N(7)—C(8), and N(7)—C(9); relatively short valence bonds C(1)=C(2), C(3)=C(4), C(5)=C(6), and C(6)—N(7); and eleven C—H bonds), small differences obtained from the results of MP2/4Z quantum-chemical calculations (see Table 1) were kept constant. The other three groups of parameters

Table 1. Geometric parameters of molecule **3** calculated by different methods

Parameter	HF/6-31G(d)	B3LYP/6-31G(d)	PBE/3Z	MP2/3Z	MP2/4Z
Distance			*d*/Å		
C(1)—C(5)	1.462	1.460	1.459	1.449	1.447
C(4)—C(5)	1.464	1.461	1.458	1.448	1.445
C(2)—C(3)	1.457	1.451	1.448	1.439	1.436
N(7)—C(8)	1.448	1.455	1.457	1.448	1.446
N(7)—C(9)	1.444	1.453	1.455	1.446	1.444
C(5)=C(6)	1.352	1.374	1.381	1.377	1.376
C(1)=C(2)	1.342	1.365	1.373	1.372	1.370
C(3)=C(4)	1.344	1.369	1.377	1.377	1.374
C(6)—N(7)	1.353	1.357	1.355	1.342	1.339
C(1)—H	1.130	1.085	1.088	1.080	1.080
C(8)—H	1.139	1.096	1.097	1.087	1.086
Angle			φ/deg		
C(1)—C(5)—C(6)	120.8	120.4	120.2	119.6	119.5
C(4)—C(5)—C(6)	133.9	133.4	133.3	133.5	133.3
C(2)—C(1)—C(5)	108.9	108.4	108.3	108.1	108.1
C(1)—C(2)—C(3)	108.3	108.4	108.4	108.4	108.4
C(2)—C(3)—C(4)	109.6	109.3	109.3	109.3	109.4
C(3)—C(4)—C(5)	107.9	107.7	107.5	107.3	107.3
C(1)—C(5)—C(4)	105.4	106.1	106.5	106.9	106.9
C(5)—C(6)—N(7)	131.8	130.9	130.7	129.9	129.9
C(6)—N(7)—C(8)	119.0	120.2	120.1	120.5	120.5
C(6)—N(7)—C(9)	121.6	122.0	122.2	121.4	121.4
C(8)—N(7)—C(9)	116.5	116.8	116.7	117.1	117.1
C(5)—C(6)—N(7)—C(8)	−161.8	−167.2	−168.7	−168.4	−168.5
C(5)—C(6)—N(7)—C(9)	1.923	0.78	0.11	0.19	0.05
C(4)—C(5)—C(6)—N(7)	5.1	6.3	5.7	5.97	5.92

included the C(1)—C(5)—C(6), C(5)—C(6)—N(7), and C(5)—C(6)—N(7)—C(8) angles. Small cross-correlation coefficients (≤0.4) between the groups confirm the possibility of reliable determination of structural parameters.

To provide the possibility for complete description of the molecular geometry of **3**, some additional assumptions of the values of angular parameters were made. Taking into account the low sensitivity of the gas-phase electron diffraction technique to small nonplanar deformations, both the dimethylamino group and the fulvene moiety including the N atom were assumed to be planar; at the same time, they could rotate about the C(6)—N(7) bond. The quantum-chemical differences (Δ) between two pairs of angles, C(1)—C(2)—C(3) and C(2)—C(3)—C(4) (Δ = 1°) and C(4)—C(5)—C(6) and C(1)—C(5)—C(6) (Δ = 13.8°) (see Table 1) were kept constant. The latter Δ value seems to be overestimated; however, the plot of

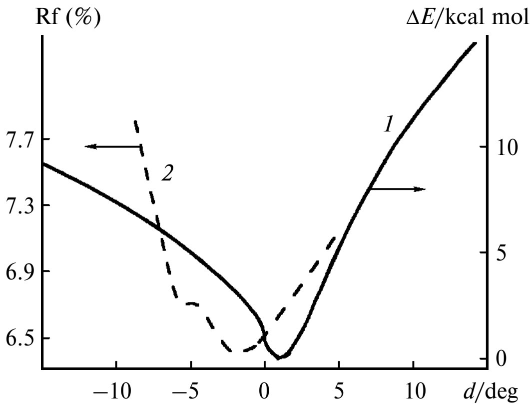

Fig. 3. Internal energy (Δ*E*) (*1*) and reliability factor (Rf) (*2*) as functions of the pyramidality of the nitrogen atom, *d* (negative *d* values were assigned to the inverted conformation of the dimethylamino group).

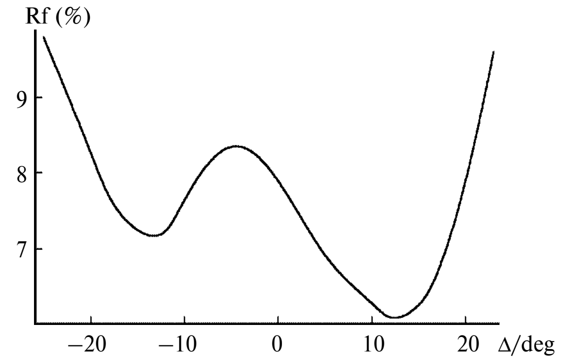

Fig. 4. Reliability factor (Rf) as function of the difference (Δ) between the angles C(4)—C(5)—C(6) and C(1)—C(5)—C(6).

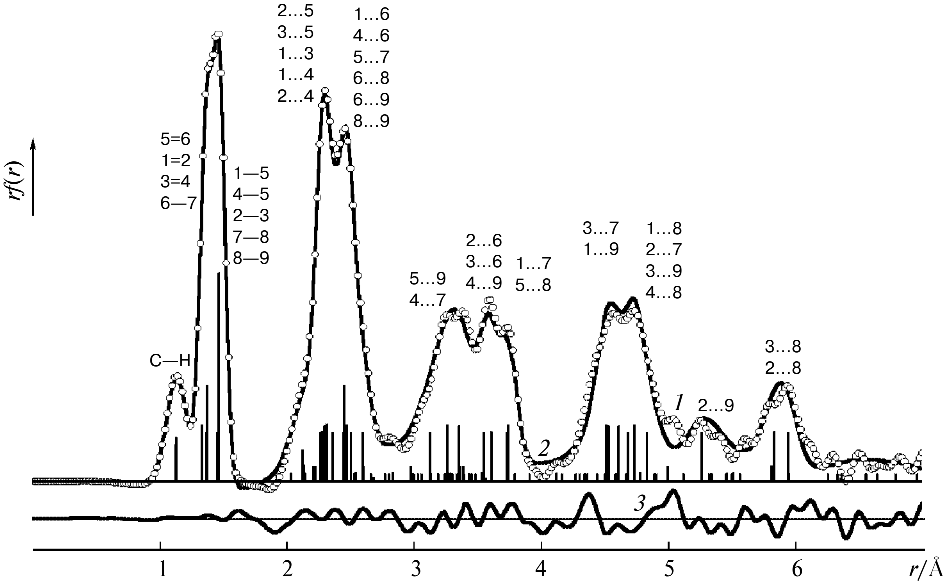

Fig. 5. Experimental (*1*) and theoretical (*2*) radial distribution curves (*rf*(*r*)), which characterizing the distribution density of internuclear distances *r* in the 6-(*N*,*N*-dimethylamino)fulvene molecule (**3**), and the difference curve (*3*). Numerals denote the numbers of atoms in molecule **3**.

the reliability factor Rf *vs.* Δ (Fig. 4) confirms its correctness.

The orientations of H atoms of the Me groups also were the same as those obtained from quantum-chemical calculations.

The vibrational amplitudes and shrinkage corrections were calculated following a known procedure[17] using the force field obtained from the B3LYP/6-31G(d) quantum-chemical calculations. These values were used as constants. For the parameters to be refined, the triple RMS deviation is given in parentheses.

Results and Discussion

The low symmetry of molecule **3** causes the appearance of a large number of close-lying terms; however, the assignment of peaks of the radial distribution curve (Fig. 5) presents no problems. The partially resolved peak at 2—3 Å is composed of the contributions of the endocyclic (on the left) and non-cyclic (on the right) geminal distances. The vicinal *cis*- and *trans*-terms (on the left and on the right, respectively) contribute largely to the peak at 3—4 Å. The peak at 4—5 Å is composed of the contributions of

Table 2. Structural parameters of molecule **3** obtained from experiments and MP2/4Z calculations (distances/Å, angles/deg, and vibrational amplitudes *U*)

Distance	Calculation	Experiment*	Ref. data[9]	*U*/Å
C(1)—C(5)	1.447	$1.469(2)^{\text{I}}$	1.470(1)	0.0485
C(4)—C(5)	1.445	$1.467(2)^{\text{I}}$	1.470(1)	0.0488
C(2)—C(3)	1.436	$1.458(2)^{\text{I}}$	1.476(2)	0.0473
N(7)—C(8)	1.446	$1.466(2)^{\text{I}}$	—	0.0482
N(7)—C(9)	1.444	$1.466(2)^{\text{I}}$	—	0.0481
C(5)=C(6)	1.376	$1.374(2)^{\text{II}}$	1.349(1)	0.0430
C(1)=C(2)	1.370	$1.368(2)^{\text{II}}$	1.355(1)	0.0433
C(3)=C(4)	1.374	$1.372(2)^{\text{II}}$	1.355(1)	0.0436
C(6)—N(7)	1.339	$1.337(2)^{\text{II}}$	—	0.0435
C(1)—H	1.080	$1.130(8)^{\text{III}}$	1.079(1)	0.0751
C(8)—H	1.086	$1.136(8)^{\text{III}}$	—	0.0756

Angle	Calculation	Experiment*	Ref. data[9]
C(1)—C(5)—C(6)	119.5	$119.3(4)^{\text{IV}}$	126.7(1)
C(4)—C(5)—C(6)	133.3	133.1	126.7(1)
C(2)—C(1)—C(5)	108.1	107.1	107.2
C(1)—C(2)—C(3)	108.4	109.0	109.0
C(2)—C(3)—C(4)	109.4	110.0	109.0
C(3)—C(4)—C(5)	107.3	106.4	107.2
C(1)—C(5)—C(4)	106.9	107.6	106.6
C(5)—C(6)—N(7)	129.9	$132.8(1)^{\text{V}}$	—
C(6)—N(7)—C(8)	120.5	120.8	—
C(6)—N(7)—C(9)	121.4	121.7	—
C(8)—N(7)—C(9)	117.1	117.4	—
C(5)—C(6)—N(7)—C(8)	−168.5	$-143.6(8)^{\text{VI}}$	—
C(5)—C(6)—N(7)—C(9)	0.05	$36.4(8)^{\text{VI}}$	—
C(4)—C(5)—C(6)—N(7)	5.9	0.0	—

Note. The Roman superscripts I—VI denote the group numbers of the varied parameters. Rf = 6.2%.

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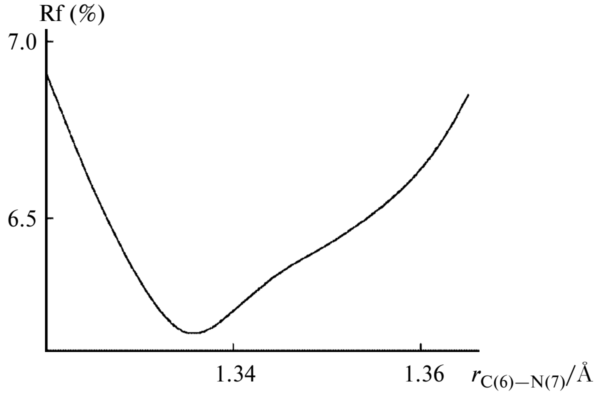

Fig. 6. Reliability factor (Rf) as function of the C(6)—N(7) internuclear distance ($r_{C(6)-N(7)}$).

the distances between the atoms separated by four bonds, while the distances between the C atoms separated by five bonds contribute to the peak in the region 5—6 Å.

Comparison of the bond lengths in the molecule under study and in the unsubstituted fulvene (Table 2) indicates a trend to equalization of the lengths of the conjugated bonds upon introduction of the dimethylamino group. However, calculations with the conjugated carbon—carbon bonds of equal lengths cause a substantial increase in the Rf value up to 18%.

Noteworthy is the unusually short internuclear distance $r_{C(6)-N(7)}$ = 1.337(2) Å obtained from gas-phase electron diffraction experiments (*cf.* r_{C-N} = 1.451(3) Å for trimethylamine**[16]** and 1.407(3) Å for aniline**[18]**). This is to a great extent due to the initial calculated value (see Table 1, $r_{C(6)-N(7)}$ = 1.339 Å), which predetermined constant values of the small differences between the close values of geometric parameters. At the same time, assessment of the sensitivity of the gas-phase electron diffraction technique to the changes in this bond length with variation of all other parameters (Fig. 6) confirmed correctness of the quantum-chemical estimate of the $r_{C(6)-N(7)}$ internuclear distance.

Calculations with all the basis sets employed (see Table 1) unambiguously point to a nearly planar equilibrium structure of molecule **3**, which is consistent with the concept of conjugation and with the presence of an additional stabilizing factor, namely, a favorable *cis*-arrangement of the N(7)—C(9) and C(5)=C(6) bonds despite the eclipsed arrangement of the N(7)—C(8) and C(6)—H bonds and unfavorable arrangement of some H atoms of the methyl and methyne groups ($r_{H...H}$) ≈ 2.1—2.2 Å). When the data of gas-phase electron diffraction experiments were checked for consistency with the planar molecular model, a Rf value of 8.8% was obtained. Rotation of the planar dimethylamino group by 36° markedly reduces the Rf value down to 6.2%. Calculations with allowance for the pyramidality corresponding to the quantum-chemical values of the C—N—C angles led to a minor decrease in the Rf value (down to 6.0%).

By and large, both the gas-phase electron diffraction data and the results of quantum-chemical calculations point to pronounced flattening of the dimethylamino group, thus indicating a conjugation between the lone electron pair of the N atom and the π-system of the fulvene ring.

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