Organic and Biological Chemistry

Evidence against Nonclassical Aromaticity in Hydrogen-Bonded Systems. 6-Aminofulvene-2-aldimines

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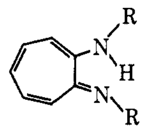
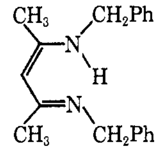
Abstract: 6-Aminofulvene-2-aldimines are easily prepared as yellow or red crystalline compounds from 6-dimethylaminofulvene. A study of their physical properties shows that in these systems an intramolecular hydrogen bond exists, through which a very fast tautomeric proton exchange takes place. From the physical evidence it is deduced that nonclassical aromaticity due to delocalization of electrons through the hydrogen bond does not exist in these and related systems.

The interest in the properties of hydrogen bonds, evidenced both by experimental and theoretical work, has recently lead to some speculation and discussion about the interpretation of intramolecular N–H···N-bonded systems in terms of nonclassical aromaticity: *e.g.*, the N,N′-disubstituted 1-amino-7-imino-1,3,5-cycloheptatrienes[1] (I) as well as 2-benzylamino-4-benzylimino-2-pentene[2] (II) have been postulated to exhibit nonclassical aromaticity in the sense of cyclic delocalized π-electron systems (with ten and six π electrons, respectively), in which the chelate proton rests in a position equidistant from both nitrogens. II has subsequently been shown[3] not to exhibit any unusual properties that might make the assumption of a novel electronic interaction through the N–H···N bond necessary. An analysis of the crystal and molecular structure of I, R = CH_3, however, has been interpreted as proof for a symmetrical structure.[4] Although the experimental X-ray data show two density maxima (indicative of a double-well potential) for the chelate proton, the absence of large tangential movements of the ring nuclei was considered to rule out a fast tautomeric equilibrium and taken as evidence for the presence of a delocalized ten π-electron system.



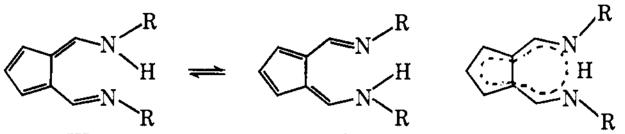
I, R = H, alkyl, aryl



II

The discussion about this phenomenon can be reduced to the question of whether the two energetically equivalent forms A and B (Figure 1 a,b) are separated by an activation barrier[5] (Figure 1a) or whether the resonance-stabilized form R (Figure 1b), in which the chelate proton would assume an equilibrium position, is the only existing one. For nonequivalent forms A and B (Figure 1c,d), the situation is similar. As has been shown by a calculation of the Pariser–Parr–Pople type[6] for the symmetrical pyridinium–pyridine pair, the shape of the potential well depends on the distance between the nitrogen atoms in such a way that N–N distances below 2.2 Å favor a single well potential while distances above 2.5 Å give rise to two distinct wells. The observed[7] distance between the nitrogen atoms (about 2.45 Å) in I, R = CH_3, falls into the area where the transition from double- to single-well potentials might occur.

6-Aminofulvene-2-aldimines (III) appear to be good model compounds for the investigation of the bonding situation in such chelates. Inspection of Dreiding models or the geometric construction from a regular five-membered ring and an exocyclic angle of 120° with all bond lengths = 1.40 Å predicts N–N distances below 2.0 Å.[8] The dipole moments of the aminofulvenealdimines are expected to point away from the nitrogens with the negative end of the dipole at the five-membered ring. It is of interest to compare this to the dipole moments found in the aminotroponimines (I, R = CH_3; μ = 1.24 D), which have been shown to have the negative end at the seven-membered ring.



IIIa IIIb IIIc

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(1) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Amer. Chem. Soc.*, **83**, 3125 (1961).

(2) L. C. Dorman, *Tetrahedron Lett.*, 459 (1966).

(3) E. Daltrozzo and K. Feldmann, *Ber. Bunsenges. Phys. Chem.*, **72**, 1140 (1968); *Tetrahedron Lett.*, 4938 (1968).

(4) P. Goldstein and K. N. Trueblood, *Acta Crystallogr.*, **23**, 148 (1967).

(5) Whether in this case the conversion A ⇄ B is achieved by proton jump or by tunnelling will not be considered in this paper. These aspects have been discussed by J. Brickmann and H. Zimmermann [*Ber. Bunsenges. Phys. Chem.*, **71**, 160 (1967); *J. Chem. Phys.*, **50**, 1608 (1968); see also H. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, **3**, 157 (1964)] and R. Rein and F. E. Harris, *J. Chem. Phys.*, **42**, 2177 (1965).

(6) J. R. Sabin, *Int. J. Quantum Chem.*, **2**, 23 (1968).

(7) Extrapolated from ref 4. For II, R_{NN} = 2.4 A is estimated.

(8) This distance could easily be enlarged by stretching the central C–C bond (C–C distance = 1.48 Å gives N–N distance 2.15 Å). The molecular structure of these compounds has so far not been determined. Unsuccessful attempts to prepare metal chelates of III, R = CH_3, Ph, point toward close proximity of the nitrogen atoms.

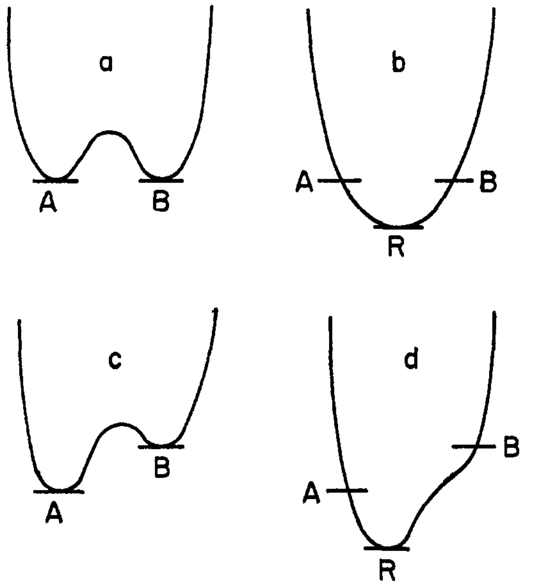


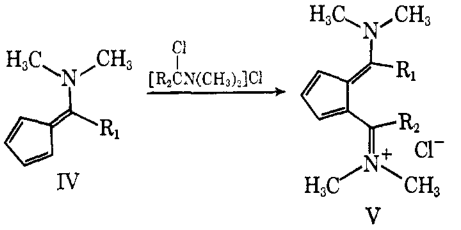
Figure 1. Double-well and single-well potentials for (a) equivalent or (c) unequivalent tautomers and (b) symmetrical or (d) unsymmetrical resonance stabilized structures.

This was interpreted[1] as additional proof for the existence of an unusual bonding situation[9] in I.

It was also expected that in the aminofulvenealdimines the two exocyclic C–H protons would couple with the N-H hydrogen in such a way that the nmr spectra would provide more detailed information about the symmetry of such hydrogen-bonded systems.

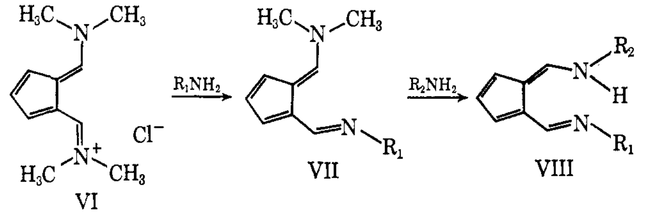
Results

Preparation. 6-Dimethylaminofulvenes (IV) can be obtained in good yields from sodium cyclopentadienide and the complex formed by heating the respective N,N-dimethylamide with dimethyl sulfate.[10] Alternative methods using the corresponding N,N-dimethylaminoethoxymethylium fluoroborates have been reported.[11] Electrophilic substitution of the 6-dimethylaminofulvenes occurs in the 2 position.[12] Thus, their reaction with the Vilsmeier complex from N,N-dimethylamides and phosgene or oxalyl chloride[10] leads to 6-dimethylaminofulvene-2-N,N-dimethylaldimmonium chlorides (V), which in most cases can be isolated as yellow solids. For the present work, the unsubstituted immonium salt (VI) was used throughout.[13] VI reacts with ammonia or primary aliphatic and aromatic amines to form the 6-aminofulvene-2-aldimines (VIII).[14] This reaction proceeds with the formation of 6-dimethylaminofulvene-2-aldimines (VII) as true intermediates, which can be isolated if R_1 is an aromatic or larger aliphatic group. Thus, it is possible to obtain "unsymmetrical" ($R_1 \neq R_2$) as well as "symmetrical" ($R_1 = R_2$) aminoimines. Except for the parent compound (VIII, $R_1 = R_2 = H$), obtained from the reaction of VI with ammonia, all aminoimines are stable, yellow or red, well-crystallized solids. The pale yellow plates of VIII, $R_1 = R_2 = H$, decompose rapidly with elimination of NH_3 to form red polymers of unknown structure. This compound can, however, be treated with ethyl chloroformate in the presence of tertiary amines to form III, $R_1 = R_2 = COOC_2H_5$. The aminoimines are sensitive to light and to some degree toward air. They are stable against cold dilute acids and bases, acting as true bases themselves since they can be extracted from ether solution into dilute HCl and from the neutralized solution again with ether. However, VIII, $R_1 = R_2 = CH_3$, easily hydrolyzes in boiling aqueous methanol, precipitating the 6-methylaminofulvene-2-aldehyde as pale yellow crystals upon cooling, hydrolysis of which with NaOH leads to the anion of 6-hydroxyfulvene-2-aldehyde. In contrast, the symmetrical *t*-butyl and phenyl derivatives are stable even toward boiling MeOH–water containing a catalytic amount of NaOH.[15] The stability of the aminoimines does not suffice to allow a Vilsmeier-type electrophilic substitution. An attempt to formylate VIII, $R_1 = R_2 = Ph$, at −70° resulted in extensive decomposition, and only a fraction of the starting material could be recovered. In this way, the aminoimines can be compared to the 5-aza- and 5,7-diazaazulenes.[16]



IV

V



VI

VII

VIII

Physical Properties. Dipole moments were determined for the aminoimines with $R_1 = R_2 = CH_3$ (VIIIb) and $R_1 = R_2 = COOC_2H_5$ (VIIIf) to prove the direction of the polarization. The results (VIIIb, $\mu = 3.27$ D; VIIIf, $\mu = 1.89$ D) confirm that the negative end of the dipole is at the five-membered ring.

The electronic spectra of the aminoimines generally show three structureless areas of absorption in the regions around 260 nm (ϵ 30,000), 350 (15,000), and 390 (10,000) (Table II). There is little difference between the uv spectra of 6-aminofulvene-2-aldimine, 6-aminofulvene-2-aldehyde, and 6-hydroxyfulvene-2-aldehyde[13] (Table III). The electronic spectra of the

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(9) This is the expected direction, if both the aminotroponimines and their isomers, the aminofulvenealdimines, are regarded as vinylog amidines, for which high electron densities in the center of the chain are generally calculated.

(10) a, R = H: K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *Org. Syn.*, 47, 52 (1967); *Justus Liebigs Ann. Chem.*, 661, 52 (1963); b, R = CH_3, NMe_2: K. Hafner, G. Schulz, and K. Wagner, *ibid.*, 678, 39 (1964); c, R = Ph: U. Müller-Westerhoff, Dissertation, Darmstadt, 1967.

(11) H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt, and J. Spille, *Chem. Ber.*, **89**, 2060 (1956); A. P. Downing, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. B*, 111 (1969).

(12) K. Hafner and K. H. Vöpel, *Angew. Chem.*, 71, 672 (1959).

(13) VI can be hydrolyzed to form the 6-hydroxyfulvene-2-aldehyde (ref 10), which has been the subject of a spectroscopic investigation (K. Hafner, H. A. E. Kramer, H. Musso, G. Ploss, and G. Schulz, *Chem. Ber.*, 97, 2066 (1964)) of its O–H···O bond.

(14) Subsequently called "aminoimines" for brevity.

(15) The difference between the methyl- and *t*-butylaminoimines in their stability toward nucleophilic agents is not surprising in view of the different steric demands of the alkyl substituents.

(16) U. Müller-Westerhoff and K. Hafner, *Tetrahedron Lett.*, 4341 (1967).

Table I. 6-Aminofulvene-2-aldimines

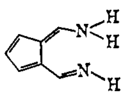
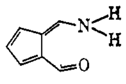
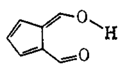
				Calcd				Found			
VIII	R_1	R_2	Mp, °C	C, %	H, %	N, %	Mol wt	C, %	H, %	N, %	Mol wt
a	H	H	86	69.97	6.71	23.32	120.16	70.41	6.85	23.05	126[a]
b	CH_3	CH_3	85	72.94	8.16	18.90	148.20	72.92	8.26	19.08	148
c	$C(CH_3)_3$	$C(CH_3)_3$	95	77.53	10.41	12.06	232.38	77.55	10.45	12.09	228
d	C_6H_{11}	C_6H_{11}	121	80.23	9.92	9.85	284.45	80.23	9.76	9.95	278
e	C_6H_5	C_6H_5	100	83.79	5.92	10.29	272.35	83.53	5.97	10.12	273
f	$COOC_2H_5$	$COOC_2H_5$	133	59.08	6.10	10.60	264.27	59.39	5.92	10.45	260
g	CH_3	$C(CH_3)_3$	52	75.74	9.54	14.72	190.29	75.65	9.48	14.72	184
h	C_6H_{11}	$C(CH_3)_3$	98	79.02	10.14	10.84	258.41	79.06	10.15	11.07	254
i	C_6H_5	$C(CH_3)_3$	99	80.91	7.99	11.10	252.37	80.88	7.90	10.99	246

[a] Polymerization with loss of ammonia occurs rapidly.

Table II. Electronic Spectra of N,N′-Disubstituted Aminofulvenealdimines

VIII	R_1	R_2	λ_{max} (nm) (in hexane)	ϵ	λ_{max} (nm) (in MeOH)	ϵ
b	CH_3	CH_3	265	22,700	264	21,600
			328	sh		
			345	13,450	340	11,950
			384	6,950	391	10,550
c	t-C_4H_9	t-C_4H_9	264	24,200	263	24,300
			328	sh		
			345	13,100	340	14,250
			382	7,500	380	8,980
d	C_6H_{11}	C_6H_{11}	266	25,800	265	30,700
			330	sh		
			347	15,200	340	14,250
			384	7,850	380	9,680
e	C_6H_5	C_6H_5	240	12,900	239	12,900
			286	32,600	286	31,900
			299	29,300	297	29,800
			377	17,250	373	17,300
			385	17,350	383	17,200
			439	13,400	437	14,100
f	$COOC_2H_5$	$COOC_2H_5$	267	28,700	305	26,300
			341	14,050		
			351	13,500	349	2,660
			425	9,350	395	1,290
g	CH_3	t-C_4H_9	268	25,800	266	24,000
			330	sh		
			346	14,920	338	12,400
			385	8,040	385	8,600
h	C_6H_{11}	t-C_4H_9	264	25,000	264	25,300
			329	sh		
			346	14,700	348	13,200
			386	7,030	385	9,160
i	C_6H_5	t-C_4H_9	279	33,330	276	29,700
			345	11,060	342	11,720
			353	sh		
			420	9,740	416	9,460

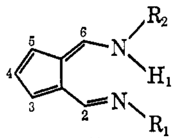
Table III. Ultraviolet Spectra of Hydrogen-Bonded Fulvenes in n-Hexane [λ_{max} nm (ϵ)]

	376 (5,430)	332 (11,200)	256 (20,300)
	386 (7,220)	327 (11,800)	250 (22,000)
	393 (5,600)	317 (9,800)	243 (19,500)

aminoimines and the aminotroponimines [I ($R = CH_3$) has[1] λ_{max} 263 nm (ϵ 17,800), 346 (8650), 360 (10,100), and 418 (6820)] show an obvious similarity. A proof for the presence of an intramolecular hydrogen bond in the aminoimines can be found in the solvent independence of their spectra.[17] For the on-nitrogen alkyl-substituted aminoimines a strong bathochromic shift of the first absorption band is observed in methylene chloride containing a trace of free HCl. This band also strongly increases in intensity while the second band decreases (VIIIb has λ_{max} nm (ϵ) 415 (15,800), 349 (11,300), and 262 (22,200)). The phenyl- and ethoxycarbonyl-substituted aminoimines exhibit no such shift, due to a lesser basicity of the nitrogens in these compounds. In dilute HCl VIIIb has λ_{max} 400 nm (27,500) and 265 (23,000).

Generally, much can be learned about the structure of hydrogen-bonded systems from their infrared spectra. However, the ir spectra of the aminoimines present little information. The presence of the hydrogen bond is shown as a broad and unstructured absorption between 3000 and 2250 cm^{-1}. Upon exchange of the chelate proton against deuterium, this band shifts to the 2200- to 1800-cm^{-1} region ($\nu_H/\nu_D = 1.3$).

Of far greater importance in determining the bonding situation in the aminoimines are their nmr spectra. The data obtained at ambient probe temperature are summarized in Table IV, in which the numbering of the protons[18] refers to formula IX.



IX

The spectra of the aminoimines with $R_1 = R_2$ show no obvious evidence against a symmetrical structure with the chelate proton in the center of the N–H···N bond. Only one signal for the substituents is found. Protons 5 and 3 appear as a doublet through coupling with the proton in position 4 (triplet, $J = 4$ Hz). Protons 6 and 2 form a doublet while the chelate proton 1 appears as an only slightly broadened (width at half-height = 4 Hz) low-field triplet with $J = 7$ Hz. That proton 1 indeed couples with *both* exocyclic hydrogens was shown by deuterium exchange (for the N–D compound the signal for protons 2 and 6 is a singlet; Figure 2 for $R_1 = R_2 =$ Ph) and by spin

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[17] The only exception is VIIIf, in which the ethoxycarbonyl groups are presumably solvated by polar solvents to such an extent that the aldimine group is no longer coplanar with the rest of the molecule. The spectrum of VIIIf in MeOH indeed resembles the spectra of N-substituted 6-aminofulvenes.

[18] For clarity, a numbering system different from the usual one is employed here.

Table IV. Nmr Spectra of 6-Aminofulvene-2-aldimines at 37° [a]

VIII	H_1	H_2	H_6	H_3	H_5	H_4	R_1 R_2	Solvent
a	−2.7 b	1.95 d (12)		3.12 d (4)		3.67 t (4)	+2.7 b	$CDCl_3$
b	−3.03 b	2.44 bs		3.43 d (4)		3.92 t (4)	6.90 s	CCl_4
c	−3.4 b	2.16 d (7)		3.38 d (4)		3.88 t (4)	8.64 s	CCl_4
d	−3.4 b	2.36 d (7)		3.46 d (4)		3.96 t (4)	6.95 b, 8.4 b	CCl_4
e	−5.33 t (7)	1.96 d (7)		3.11 d (4)		3.70 t (4)	2.86 m	CCl_4
f	−4.72 t (7)	1.44 d (7)		2.86 d (4)		3.42 t (4)	5.86 q (8), 8.62 t (8)	$CDCl_3$
g	−3.27 b	2.16 s	2.50 d (9)	3.43 m	3.52 m	3.98 t	6.72 s, 8.68 s	CCl_4
h	−3.43 b	2.16 d (3)	2.50 d (11)	3.49 m		3.98 t	7.0 b, 8.2 b, 8.66 s	CCl_4
i	−3.65 bd (13)	1.76 s	2.51 d (13)	3.16 m	3.40 m	3.85 t (4)	2.94 m, 8.60 s	CCl_4

[a] Chemical shifts in τ units, coupling constants (Hz) in parentheses (b = broad absorption, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

decoupling.[19] With all "symmetrical" ($R_1 = R_2$) aminoimines these signals become increasingly sharper at lower temperatures, while upon warming another effect (see below) plays a dominant role: the doublets collapse to singlets while the N–H signal broadens. For $R_1 = R_2 = CH_3$ this is the case already at room temperature (coalescence at −27°). The spectrum of this compound does not show any broadening of the methyl singlet which might be due to H–N–CH_3 coupling.[20] This and the relative sharpness of the N–H peaks[21] speak for a very fast tautomeric exchange.

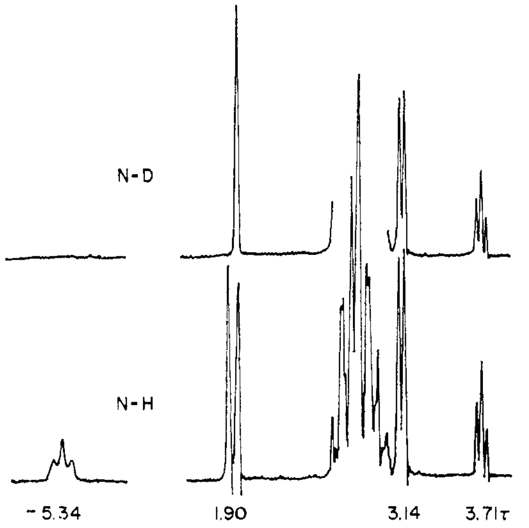

Figure 2. Nmr spectrum of VIIIe in CCl_4. Upper curve after deuterium exchange in CH_3OD.

Significant differences are found in the nmr spectra of the "unsymmetrical" ($R_1 \neq R_2$) aminoimines VIIIg–i. In VIIIi a situation similar to the 6-methylaminofulvene-2-aldehyde (i, ref 20) is encountered. Between +40 and −120°, H_2 appears as a sharp singlet and H_6 as a sharp doublet with a coupling constant of 14 Hz, which is also shown by the N–H proton at lower temperatures. Below −60° the N–H signal becomes increasingly sharper, showing that a fast exchange indeed takes place.

In VIIIg and VIIIh the alkyl substituents have a comparable influence on the total system but still leave the two tautomers energetically different. The nmr spectrum of VIIIg in THF-d_8–20% CS_2 at 37° shows a slightly broadened singlet at τ 2.11 for H_2 and a broadened doublet (with 9 Hz approaching the coalescence point) for the proton in position 6 at τ 2.33. At −10° the singlet begins to broaden, while the doublet (which at lower temperatures eventually merges with the singlet) sharpens further. Below −70° the singlet sharpens as well. What happens here can be seen more clearly in the nmr spectrum of VIIIh with R_1 = cyclohexyl and R_2 = *t*-butyl in THF-d_8–20% CS_2 at lower temperatures (Figure 3). In this compound the two substituents are not only comparable in their electronic influence but also comparable in size. In the temperature range from +32 to −70°, two doublets with different coupling constants can be observed for the two exocyclic protons. At −37°, these doublets have $J_{1,6}$ = 11 Hz and $J_{1,2}$ = 3 Hz. The doublet for H_2 coalesces again at −80° to a singlet, while the coupling constant $J_{1,6}$ increases to 13 Hz. The signal for H_1 sharpens at lower temperatures and shifts to lower field strengths.

Discussion

The nmr spectra of the aminoimines can be consistently interpreted in the following way. If J_1' and J_2' are the "true" coupling constants (*e.g.*, $J_{1,2}'$ and $J_{1,6}'$) in the two forms of a tautomeric system in which a fast (relative to the nmr time scale) exchange takes place and for which the two "observed" coupling constants J_1 and J_2 are found, then eq 1 must hold, unless an external influence interferes with the exchange. Equation 1 can be written[22] as eq 2a and 2b, in which k

$$J_1 + J_2 = J_1' + J_2' \qquad (1)$$

$$J_1 = k(J_1' + J_2') \qquad (2a)$$

$$J_2 = (1 - k)(J_1' + J_2') \qquad (2b)$$

may be regarded as a population factor, representing the fraction of molecules in one of the tautomers.

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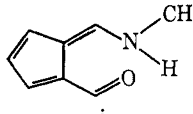
[19] Irradiation at the center of the low-field triplet causes the collapse of the doublet for the exocyclic protons to a singlet. Irradiation of the center of the doublet reduces the N–H signal to a singlet (width at half-height = 4 Hz).

[20] In 6-methylaminofulvene-2-aldehyde (i) the proton in position 6 appears as a doublet (J = 14 Hz for the *trans*-enamine coupling) and a sharp singlet is observed for the aldehyde proton. H–N–CH_3 coupling causes the CH_3 signal to split into a doublet (J = 5 Hz). At low temperatures (−80°), these two coupling constants can be observed for the N–H proton as well. The tautomeric form (ii) is energetically much less favored.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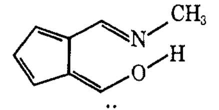

ii

[21] The broadening of a N–H signal due to the nuclear quadrupole moment of N can be reduced by a fast exchange.

[22] Addition of eq 2a and 2b is proof for their identity with eq 1.

For the case that only a small fraction of molecules exists in one of the tautomeric forms ($k \rightarrow 0$), $J_1 = 0$ and $J_2 = J_1' + J_2'$. Such a case appears to be exemplified by VIIIi with R_1 = Ph and R_2 = *t*-Bu, for which $J_{1,2} = 0$ and $J_{1,6}$ = 14 Hz are found at −60°. This allows the conclusion that for the =CHNRH···NR=CH– system in the aminoimines as a class $J_1' + J_2'$ = 14 Hz.

For the aminoimines with $R_1 = R_2$, $k = 0.5$ since both tautomers are equivalent. From eq 2a and 2b the observed coupling constants for these cases should be $J_1 = J_2 = 0.5(J_1' + J_2')$ = 7 Hz, which is the value found experimentally throughout the series at lower temperatures down to −120°, the limit to which measurements were possible.[23] At higher temperatures, the relation expressed in eq 1, 2a, and 2b no longer holds, since the condition that no external influence interferes with the exchange is no longer fulfilled. At these temperatures, rotation about the C_{sp^2}–N bonds begins to play a role. Rotation of 180° brings the amine proton into a position from which intermolecular hydrogen exchange is possible. As a consequence, the N–H signal broadens and the doublet for the exocyclic protons eventually coalesces to a singlet.[24] The coalescence temperature depends on the size of the substituents[25] and their conjugative effect.

The large chemical shifts of the N–H protons (τ −3 to −5.5) of the aminoimines are somewhat surprising, since only strongly acidic protons are usually found in this region.[26] It appears evident that the rate of proton exchange affects the position of these signals, since their shift to lower field strengths at lower temperatures is associated with a definite sharpening. This is true not only for the symmetrical but also for the unsymmetrical aminoimines.

The interesting temperature dependence of the coupling constants for H_2, H_6, and the chelate proton in VIIIh (Figure 3) can be explained in terms of a temperature dependence of the population factor *k*. From the coupling constants (3 and 11 Hz) at −13° a *k* value of 0.2 can be calculated. This can be interpreted as evidence for the existence of two tautomers rather than *one* structure with the proton at the potential minimum.

The deciding proof against the latter case comes from the nmr spectrum at still lower temperatures. Below −80° the collapse of the doublet for H_2 to a singlet is observed. At the same time the coupling constant $J_{1,6}$ increases to 13 Hz. This behavior can only be explained in terms of two distinct and energetically different tautomers (Figure 1c), of which the one lower in energy becomes more and more preferred at lower temperatures.[27] That the activation barrier between these tautomers has to be small can be deduced from the high rate of proton exchange between the tautomers, which at low temperatures[28] gives rise to a sharp doublet for the N–H proton. This finding definitively excludes the existence of only one resonance form (Figure 1d) of nonclassical aromatic character.

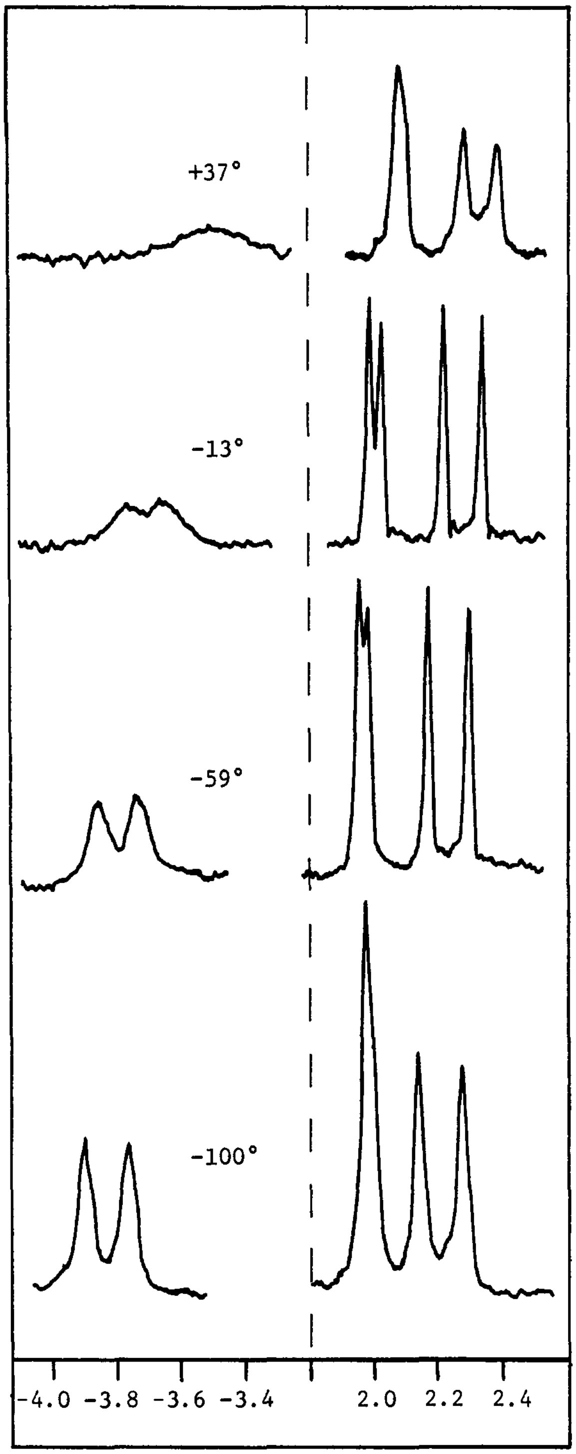


Figure 3. Nmr spectrum of VIIIh (protons 1, 2, and 6) in THF-*d* + 20% CS at various temperatures.

The term "nonclassical aromaticity" in hydrogen-bonded systems has been chosen as a synonym for the assumed interaction between the hydrogen donor and acceptor atoms, allowing a cyclic delocalization of the π-electron system. Inherent in this and any other definition of aromaticity is the postulate that the given electronic system assumes a state lower in energy than any of the limiting structures. In the case of the N–H···H hydrogen bond, these "limiting structures"

[23] Below −120° crystallization occurred in all cases.

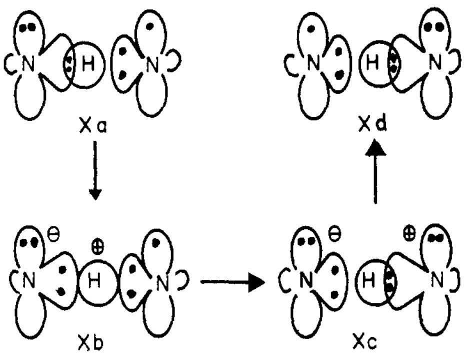
[24] The coalescence temperatures are solvent dependent. VIIIh in $CDCl_3$ shows a singlet for H-2 at ambient temperature; in CCl_4 (Table IV) it is a doublet of J = 3 Hz.

[25] Owing to the proximity of the nitrogens, the form suitable for intermolecular hydrogen exchange is sterically unfavorable.

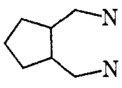
[26] An even larger shift in a related system has been described by M. Neuenschwander and H. Schaltegger *Helv. Chim. Acta*, 51, 249 (1968).

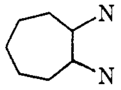
[27] For $J_{1,6}$ = 3 Hz, the population factor of eq 2b is 0.07.

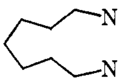
[28] That this signal is broadened at higher temperatures is a consequence of the aforementioned rotation around the C–N bonds.

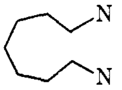


would correspond to Xa and Xd, while the stabilized form could be, in principle, realized either by interactions through the chelate hydrogen, located equidistant from the nitrogens, with participation of its $2p\pi$ AO, or by direct interaction (at short N–N distances) between the nitrogens "in spite" of the hydrogen. The importance of the $2p\pi$ AO of the hydrogen atom in the formation of strong, short hydrogen bonds has been demonstrated in calculations[29] for the F–H–F anion and postulated for several other cases.[30] Support for some interaction between the nitrogens in the aminofulvenealdimines and the aminotroponimines comes from π-SCF-LCAO-MO calculations including configuration interaction, which were carried out[31] for the four systems XI–XIV, both for symmetrical (equivalent nitrogen) and unsymmetrical structures with various values for $\beta_{NN}{}^{core}$ (0.0–0.4$\beta_{CC}{}^{core}$), corresponding to direct interactions between the two nitrogens. The results (although limited in value due to the simplifications inherent in the method) indicate some interaction of this kind to be likely, since better agreement between calculated and observed electronic spectra is obtained with nonzero values for the N–N resonance integral. Calculations for the systems with unequivalent nitrogens reproduce the spectra better than ones with symmetrical structures. The calculated bond orders for the central bonds in XI and XII are small. This, together with the found similarity of the uv spectra of the aminofulvenealdimines and the aminotroponimines, lets it appear reasonable to regard both types of compounds as vinylog amidines with very similar electronic structure, in which the central bond, except for giving these compounds a planar structure, is of minor influence. This reasoning is supported by the fact that for all four systems (XI–XIV) dipole moments directed away from the nitrogens (as found in I and VIII) were calculated.

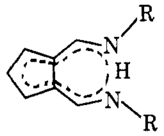

XI

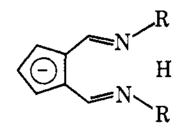

XII


XIII


XIV

Even if the assumed close proximity of the nitrogens in the aminoimines makes a direct interaction between them likely, it can be only estimated to what extent it does in fact play a role in I and VIII. It certainly would be convenient to explain the strong downfield shift of the chelate proton in the nmr spectra of the aminoimines by such an interaction.[32] The stabilizing effect of this nonbond resonance can only be small. The evidence for the existence of two distinct tautomers in VIII, presented in this paper, shows that any classical or nonclassical resonance has to have an effect smaller than the activation energy for the tautomeric exchange. This barrier may possibly be minimized (allowing an extremely fast exchange), but it remains present. This conclusion certainly rules out that structures like XV or XVI, the equivalents of which have been proposed for the aminotroponimines (K and L in ref 1), and the participation of the hydrogen $2p\pi$ AO are of importance, although a polarization as in XVI clearly might be more favored in the aminofulvenealdimines than in the aminotroponeimines. It appears more justified to regard the proton exchange in these compounds as a classical tautomeric exchange as described in Xa–d, in which the last step involves the movement of an electron "the long way" along the carbon chain. The 6-aminofulvene-2-aldimines, therefore, represent classical nonaromatic rather than nonclassical aromatic systems.


XV


XVI

Experimental Section

Uv spectra were recorded on a Cary Model 14. A Varian HA 100 instrument was used for the determination of the nmr spectra. Melting points are uncorrected. Molecular weights were determined cryoscopically in benzene.

6-Aminofulvene-2-aldimine (VIIIa). Ether (100 ml) and aqueous ammonia (70 ml) were shaken in a separatory funnel until the pressure had equalized. The immonium salt VI (2.1 g) was added and the mixture shaken rapidly. The ether layer was separated and, after drying over sodium sulfate, evaporated at a maximum of 20° on a rotary evaporator. The yellow to red residue can be recrystallized with high losses from cyclohexane by adding the boiling solvent and filtering into a cooled (ice water) flask. The pale yellow plates melt at 86° (rapid heating). The yield is 600–900 mg (50–75%).

N,N′-Dimethyl-6-aminofulvene-2-aldimine (VIIIb). Preparation was the same as for VIIIa with 40% aqueous methylamine and recrystallization from hexane gave 1.3 g (85%) of fine yellow plates, mp 85°.

6-Dimethylaminofulvene-2-(N-*t*-butyl)aldimine (VII, R_1 = *t*-Bu). To a suspension of 4.2 g of VI in 250 ml of absolute ether, 5 ml of *t*-butylamine was added and the mixture was stirred for 2 hr. The amine hydrochloride was filtered and the solvent removed under reduced pressure. Recrystallization of the yellow residue from hexane produced 3.1 g (76%) of long yellow needles, mp 159°.

Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71; mol wt, 204.32. Found: C, 76.49; H, 9.99; N, 13.76; mol wt, 203.

N,N′-Di-*t*-butyl-6-aminofulvene-2-aldimine (VIIIc). A solution of 2.5 g of VII, R_1 = *t*-Bu, in 50 ml of EtOH was refluxed with 5 ml of *t*-butylamine. After removal of the solvent, the residue was recrystallized from hexane: 2.4 g (85%), mp 95°.

N,N′-Dicyclohexyl-6-aminofulvene-2-aldimine (VIIId). A solution of 4.2 g of VI in 80 ml of absolute EtOH was refluxed with 4.0 g of cyclohexylamine for 30 min. After addition of charcoal, the solution was filtered. On cooling, crystals precipitated which were recrystallized from hexane, giving 4.9 g (83%) of fine yellow needles, mp 121°.

N,N′-Diphenyl-6-aminofulvene-2-aldimine (VIIIe). Preparation was the same as for VIIId, with 10.6 g of VI and 25 ml of aniline in

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[29] E. Clementi and A. D. McLean, *J. Chem. Phys.*, 36, 745 (1962).

[30] M. Suard, *Biochim. Biophys. Acta*, 64, 400 (1962); L. Paoloni, *Sci. Rep. Ist. Super. Sanita*, 1, 513 (1961). For a review, see S. Bratoz, *Advan. Quantum Chem.*, 3, 209 (1967).

[31] Calculations were performed on an IBM/360 Model 91 with the π-electron program PEP (U. Müller-Westerhoff, 1968). Details about the calculations are available upon request.

[32] Since the chelate proton is located closely to the N–N internuclear line, even a weak induced ring current would have a strong effect on the chemical shift of this proton.

100 ml of EtOH. Recrystallization from EtOH gave 9.4 g (69%) of VIIIe, mp 100°.

N,N′-Diethoxycarbonyl-6-aminofulvene-2-aldimine (VIIIf). To a solution of 1.2 g of VIIIa and 10 ml of triethylamine in 100 ml of absolute ether, a solution of 2.2 g of ethyl chloroformate in 10 ml of ether was added at 0°. After stirring for 30 min, the brown ether solution was washed with water and, after drying, evaporated under vacuum. The residue was recrystallized from cyclohexane, giving 1.4 g (53%) of fine yellow needles, mp 133°.

6-*t*-Butylaminofulvene-2-(N-methyl)aldimine (VIIIg). In a separatory funnel, a solution of 5.1 g of VII, R_1 = *t*-Bu, in 100 ml of ether was shaken with 75 ml of 40% aqueous methylamine. The ether layer was washed twice with water and dried. Evaporation of the solvent afforded a yellow oil, which solidified upon cooling. Recrystallization from hexane (−60°) gave 4.3 g (91%) of yellow crystals, mp 52°.

6-*t*-Butylaminofulvene-2-(N-cyclohexyl)aldimine (VIIIh). A mixture of 2.0 g of VII, R_1 = *t*-Bu, and 1.0 g of cyclohexylamine in 50 ml of MeOH was refluxed for 1 hr. Upon cooling, 2.4 g (93%) of yellow needles precipitated, which, after recrystallization from MeOH, had mp 98°. In some instances, a mixture of two crystalline forms (mp 84 and 98°) was obtained. Differential scanning calorimetry confirmed that above 84° an exothermic crystallization occurred.

6-*t*-Butylaminofulvene-2-(N-phenyl)aldimine (VIIIi). A solution of 2.0 g of VII, R_1 = *t*-Bu, and 0.95 g of aniline in 100 ml of hexane was refluxed for 1 hr. On cooling, yellow crystals precipitated which were recrystallized from hexane. The yield is 2.4 g (96%), mp 99°.

6-Methylaminofulvene-2-aldehyde (i). A solution of 1.0 g of VIIIb in 50 ml of EtOH and 30 ml of water was heated on a steam bath for 2 hr. On cooling, 0.90 g (96%) of crystals precipitated. Recrystallization from hexane gave yellow neddles, mp 71.5°.

Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36; mol wt, 135.17. Found: C, 71.26; H, 6.71; N, 10.15; mol wt, 134.

Acknowledgments. The synthesis and the physical investigations of the symmetrically substituted aminoimines were carried out in K. Hafner's laboratory at the Institut für Organische Chemie der Technischen Hochschule, Darmstadt, as part of the author's dissertation. I wish to thank Professor Hafner for his valuable advice and many discussions. I am also indebted to Mrs. L. W. Mansperger, Miss M. Woscheé, and Mr. T. T. Horikawa for their technical assistance.

Energy Transfer in Chemiluminescence.[1,2] II

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Abstract: Both 2,3-dihydro-6-[(9,10-diphenyl-2-anthryl)methyl]benzo[*g*]phthalazine-1,4-dione (**4**) and 2,3-dihydro-6-[(9-oxo-10-acridanyl)methyl]phthalazine-1,4-dione (**6**) have been synthesized. These compounds are chemiluminescent under oxidative conditions. The chemiluminescence emission spectra of **4** and **6** show that intramolecular energy transfer is occurring in these compounds. The relative chemiluminescence quantum yields, with respect to luminol (about 1.0), have been measured and are, for **4** and **6**, 0.26 and 0.08, respectively. The rate of energy transfer in compound **4** was calculated to be 2.4×10^7 sec^{-1}.

The concept that an electronically excited state can transfer its energy to a ground state of another atom or molecule, raising it in turn to an excited state, was first predicted by Franck in 1922.[3] Since that time intermolecular energy transfer has been studied extensively and it forms the basis for sensitized photochemistry.[4]

Intramolecular energy transfer also has been studied using molecules containing two nonconjugated chromophores, *i.e.* D–A. When the donor (D) is raised to an excited state by light absorption, emission is observed from the acceptor (A) portion of the molecule. Examples of this type of transfer have been reported by several groups of workers.[5–7]

In chemiluminescence, in which chemically produced electronically excited states are involved,[8,9] intermolecular energy transfer has been shown to be an important process. Examples of this process include the reaction of oxalyl chloride or oxalate esters with hydrogen peroxide in the presence of fluorescent acceptors,[10] the decomposition of dicyclohexyl peroxycarbonate in the presence of acceptors,[11] the autoxidation of tetralin in the presence of 9,10-diphenylanthracene,[12] and the decomposition of tetralin hydroperoxide in the presence of porphyrins.[13]

To observe intramolecular energy transfer in chemiluminescene, we have prepared hydrazides in which the energy-generating and light-emitting functions are separated.

The chemiluminescene of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione, **1**, 5 = NH_2) and related hydrazides (**1**) has been studied extensively.[8,9,14–18]

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(1) For paper I see E. H. White and D. F. Roswell, *J. Amer. Chem. Soc.*, 89, 3944 (1967).

(2) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 15, 1967.

(3) J. Franck, *Z. Phys.*, **9**, 259 (1922).

(4) For example, see N. J. Turro, "Molecular Photochemistry," 1st ed, W. A. Benjamin, New York, N. Y., 1967.

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(6) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, **87**, 995 (1965).

(7) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, **87**, 2322 (1965).

(8) E. H. White in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961, p 183.

(9) (a) K. D. Gundermann, "Chemilumineszenz Organisher Verbindungen," Springer-Verlag, Berlin, 1968; (b) R. F. Vassil'ev in "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press, New York, N. Y., 1967, p 305.

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