cm^{-1}; pmr (CCl_4) δ 7.14 (m, 10, aromatic), 4.83 [d, 1, $CH(OCH_3)_2$], 4.12 [d, 1, $CH(C_6H_5)_2$], and 3.17 (s, 6, OCH_3), $J_{H(1),H(2)} = 8.0$ Hz.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.18; H, 7.33.

Registry No.—I, 872-05-9; II, 30390-81-9; IV, 51936-02-8; V, 51936-03-9; VI, 563-79-1; IX, 51936-04-0; X, 51936-05-1; XI, 103-30-0; XII, 1147-17-7; XIII, 51936-06-2; XIV, 51936-07-3; XV, 3720-11-4; XVI, 645-49-8; XVII, 14156-28-6; XVIII, 51936-08-4; XIX, 3720-10-3; TTN, 13746-98-0; 2-methoxy-1-decanol, 5935-15-9; 1-methoxy-2-decanol, 5935-14-8; 2,3-dimethyl-3-methoxy-2-butanol, 51936-09-5; 2,3-dimethyl-2,3-butanediol, 76-09-5; *erythro*-1,2-diphenyl-2-methoxy-1-ethanol, 6941-71-5; *dl*-1,2-diphenyl-1,2-ethanediol, 655-48-1; *meso*-1,2-dibromo-1,2-diphenylethane, 13027-48-0; diphenylethanal, 947-91-1.

References and Notes

(1) This research was supported by NSF Grant GP-33423.

(2) R. J. Bertsch, unpublished results.

(3) A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Lett.*, 5275 (1970).

(4) A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, **95**, 3635 (1973).

(5) They noted that "the normal TTN oxidations in methanol leading to oxidative rearrangement are at times accompanied by a minor side reaction which gives varying amounts (5–15%) of glycol mononitrate esters. A careful examination of the TTN-CH_3OH oxidation of cyclohexene to cyclopentanecarboxaldehydeshowed that the mononitrate ester formed in this case was not an intermediate in the ring contraction reaction."

(6) "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 2733M.

(7) Reference 6, Spectrum No. 6826M.

(8) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967), gives for VIII δ 1.5 (s, 2, CH_3), 3.18 (s, 1, OCH_3).

(9) L. M. Soffer, E. W. Parrotta, and J. D. Domenico, *J. Amer. Chem. Soc.*, **74**, 5301 (1952).

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(13) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1955, pp 100–103.

(14) G. Berti, F. Bottari, P. L. Ferrarini, and B. Macchia, *J. Org. Chem.* **30**, 4091 (1965).

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(16) See ref 13, pp 180–181.

(17) See ref 13, pp 188–190.

Evidence Pointing to an Uncharged Homoheteroaromatic System in an Enaminoimine with an N–H–N Bridge

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Spectral and chemical evidence suggest cyclic delocalization in the ground state of 1,2-di-*tert*-octylamino-3-*tert*-octylimino-1,3-dicyanopropene-1 (**7**). A monohomopyrazole structure is proposed with a short intramolecular N–H–N bond that bridges the single interruption in the σ framework. This bond is postulated to have a potential with either a symmetrical double well or a central single well. The hydrogen atom is probably located out of the plane of the ring, thus allowing transmittal of conjugation through overlap of p orbitals on the terminal nitrogens. Electron density is expected to be relatively low on these nitrogens and high on the α carbon atoms. It is proposed that the stabilizing effect of the nitrile groups may make such a homoaromatic structure energetically favorable.

Homoaromatic systems are defined as aromatic systems in which part of the σ framework is interrupted.[1] Homoaromatic stabilization is now well recognized for a number of charged species.[2,3] Recently homoaromaticity has for the first time been demonstrated in a neutral hydrocarbon.[4]

In heterocyclics such as pyrrole and pyrazole, aromaticity implies (in a VB representation) the contribution of charge-separated ylide-like structures. This suggests the possible existence of neutral homoaromatic heterocyclic systems.

An unusual type of cyclic delocalization, reminiscent of homoaromaticity, has been proposed before for certain compounds with enaminoimine or aminotroponimine structures. Specific examples are 2-benzylamino-4-benzyliminopentene-2 [**1** $\equiv$ **2a** (or **2b**), R_1 = CH_2Ph; R_2 = CH_3][5a] and 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (**3**).[6] (See Chart I.)

Subsequently, Daltrozzo and Feldmann[5b] have shown that in **1** no unusual cyclic delocalization exists. Instead, very rapid proton exchange occurs between the nitrogen atoms of two tautomeric forms [**2a** $\rightleftharpoons$ **2b**, R_1 = $PhCH_2$; R_2 = CH_3 (Chart I)].

Furthermore, Müller-Westerhoff[7a] has recently disproven nonclassical aromaticity in 6-aminofulvene-2-aldimines (**4**, Chart I) and has extrapolated this conclusion to the structurally related aminotroponimines (**3**).

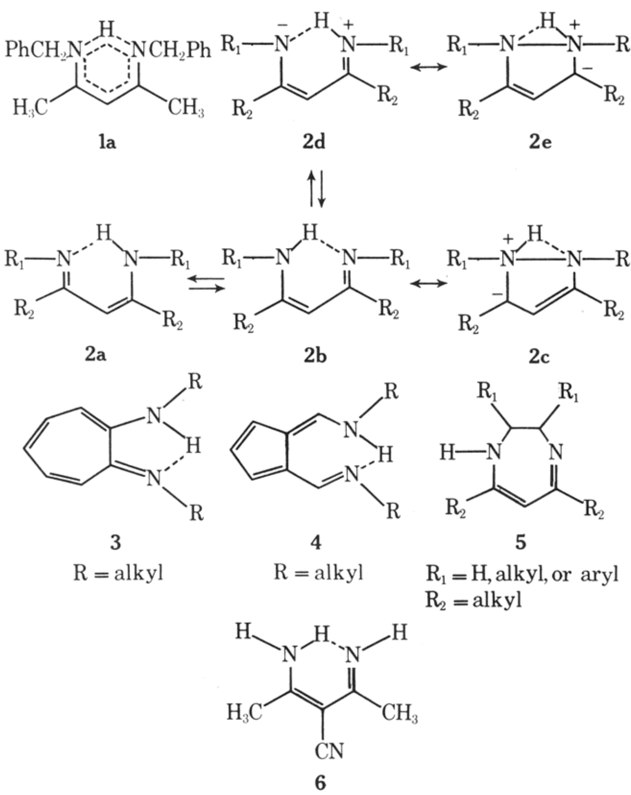
He concludes, however, that some interaction between orbitals on the two nitrogens[8] is probable "in spite of" the proton (at very small N–N distance). In essence this amounts to a homoallylic effect. Müller-Westerhoff did not consider a bent N–H–N bridge with the hydrogen out of the plane. However, for effective transmission of conjugation, the overlap must be intermediate between π and σ.[1] That is only possible when the bridging hydrogen is located out of the plane of the ring.[10]

In enaminoimines such as **1** the substituents (methyl or benzyl) on the chelated ring have been shown to be equivalent by nmr spectroscopy.[5,11a,12] Averaging of the environment must therefore be rapid relative to the nmr time scale. This implies that not only fast intramolecular proton transfer occurs but that additionally the ring atoms have to average their positions through a concerted adjustment of bond lengths.

Although these two processes must occur concurrently, and must both be fast, they need not necessarily be synchronized. Proton transfer can probably occur much faster than concerted bond length adjustment because the latter requires rehybridization at the terminal nitrogens as well as movements of the carbon and nitrogen atoms that are large relative to normal vibrational amplitudes.

The N–H–N bond in the enaminoimines may resemble the bridges in the associated imidazoles which have been investigated extensively by Zimmermann.[14] Ultrafast proton transfer—possibly by tunneling—may occur without

Chart I


1a, 2d, 2e, 2a, 2b, 2c

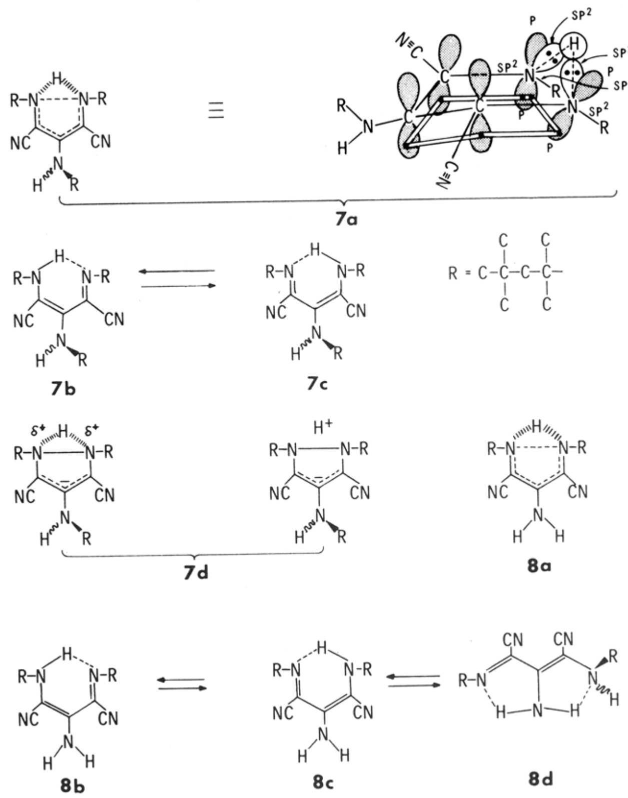
3 R = alkyl

4 R = alkyl

5 R_1 = H, alkyl, or aryl; R_2 = alkyl

6

Chart II


7a, 7b, 7c, 7d, 8a, 8b, 8c, 8d

adjustment of bond lengths, thus giving rise to rapid interconversion between a nonpolar structure **2b** and a proton-transferred structure **2d.**[15]

Homoallylic overlap between p orbitals on the nitrogens would result in the additional, bridged forms **2c** and **2e.** Owing to the distorted bond lengths, the first of these is probably of high energy and contributes little to the stability of the open nonpolar structure **2b.** The relatively undistorted **2e** may, however, stabilize the open proton-transferred structure **2d** considerably. This should tend to diminish the energy difference between **2b** and **2d** as well as the height of the separating energy barrier. Such conditions are conducive to proton delocalization (tunneling) as demonstrated by Zimmermann for the associated imidazoles.[14a]

Homoallylic interaction could thus account for an anomalously short and possibly strengthened hydrogen bridge in enaminoimines.

In the ylide-like forms **2e** and **2c** a formal positive charge resides on the heteroatom and a negative charge on the α-carbon atom. Therefore, substitution of electron-withdrawing groups on the α-carbon atoms in enaminoimines should increase stabilization. The opposite should be true for electron-donating substituents such as the methyl groups of **1.** Furthermore, certain electron-withdrawing groups may be capable of stabilizing a homoaromatic ground state with all ring atoms in intermediate positions. The amount of energy required to keep the ring atoms in these intermediate positions can be roughly estimated from a comparison with the benzene–cyclohexatriene case. The compression energy of benzene, where six bonds are involved, has been variously estimated at 27–35 kcal.[16] For enaminoimines, where only four bonds are involved, 20 kcal is a rough estimate. If cyclic delocalization is to occur, it must at least account for this amount of resonance energy.

On the basis of spectral and chemical evidence, it is proposed that this requirement may be met for 1,2-di-*tert*-octylamino-3-*tert*-octylimino-1,3-dicyanopropene-1 (**7**)[17] (Chart II). Specifically, the nmr spectrum shows evidence for the presence of a ring current; vibrational spectra indicate molecular symmetry, a high degree of equalization of bond orders in the ground state, and the absence of a mode attributable to the C=N moiety; the uv spectrum shows an anomalous "interaction band;" and protonation occurs on one of the "electron-rich" carbon atoms, bearing the nitrile groups, rather than on a relatively electron-depleted amino or imino nitrogen.

A second compound (**8**) has also been prepared which differs from **7** only through lack of a *tert*-octyl substituent on the central amino group. For **8** all available evidence suggests a classically conjugated enaminoimine structure.

If the transition from homoconjugative interaction—as may occur in **1**—to complete cyclic delocalization—as postulated for **7**—indeed depends upon transmission of electron withdrawal by the nitrile groups (see above), then the lack of homoaromaticity in **8** may be rationalized as follows.

Models of **7** and nmr evidence indicate that the effect of the bulky substituent on the central amino group is to twist the lone electron pair on nitrogen out of conjugation with the unsaturated system in the hydrogen bonded ring and consequently with the vinylic β-nitrile group. However, through the circuitous homoconjugative route, the electron demand of this nitrile group could be satisfied by the α-amino group.

In contrast, the unsubstituted central amino group in **8** can be coplanar with the ring and can provide electron density to the vinylic β-nitrile group. The correspondingly lowered demand for homoconjugative electron supply from the α-amino group may now be insufficient to support homoaromaticity. Moreover, in **8**, hydrogen bond formation between the terminal amino and imino groups (**8b** $\rightleftharpoons$ **8c,** Chart II) must compete with hydrogen bonding between these groups and the central unsubstituted amino group as in **8d** where homoaromaticity is not possible.

Since the cyclic delocalization as in **7a** requires all ring atoms to remain in intermediate positions, the N–H–N

Table I
Nmr Spectrum[a] of 7

		NH		CH_2		$C(CH_3)_2$		$C(CH_3)_3$[b]	
Solvent	Temp, °C	A	B	A	B	A	B	A	B
CCl_4	25	9.88	2.68	1.54	1.79	1.10	1.42	1.05	0.95

[a] In parts per million (δ). [b] The small difference in the positions of the A and B *tert*-butyl signals (A and B labeling as in Figure 1) may be largely of statistical origin. A model (Figure 2) shows that rotation around the single bonds in the *tert*-octyl substituents allows the A *tert*-butyl groups to enter both nitrile-deshielding zones while the B group can enter only one.

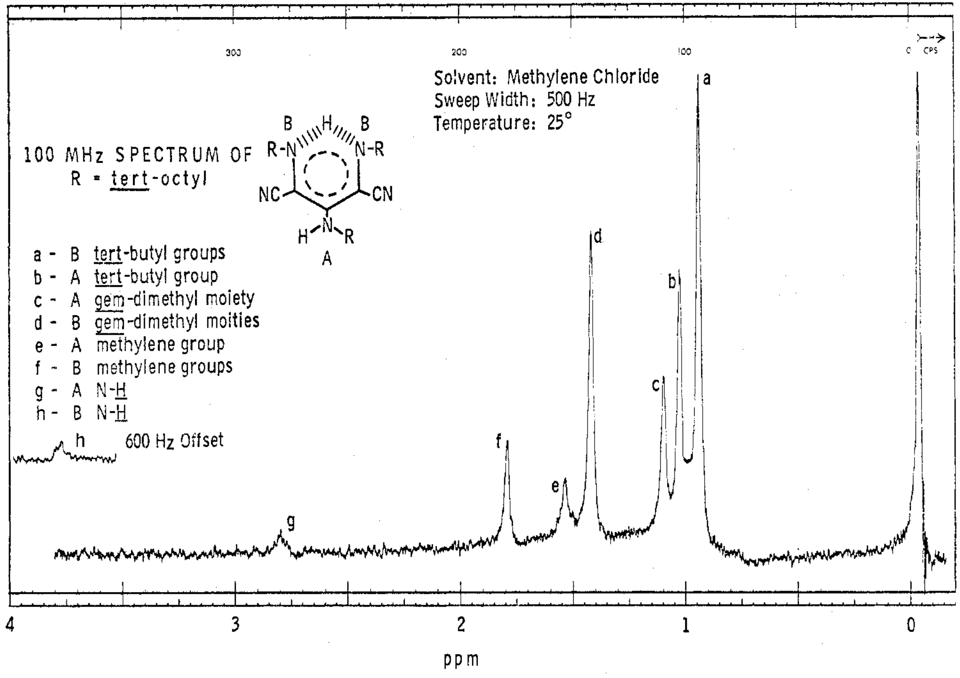


Figure 1.

bridge must be symmetrical with either two equally deep energy wells or a single central well.[18] The nature of this bridge is, however, incidental to its prime function in **7a**. This is to keep the nitrogens in close proximity so as to allow effective p-orbital overlap.

Evidence for the Structures of 7 and 8. Nmr Spectra. Nmr spectra have been reported for a few symmetrically substituted enaminoimines. In each case, the substituents were found to be magnetically equivalent. This indicates proton exchange between the nitrogens, which is fast relative to the nmr time scale.

Examples are the 1,4-diazepines[21a] (**5**), 2-benzylamino-4-benzyliminopentene-2[5] (**1**), and 2-amino-3-cyanopent-2-ene-4-imine[11a] (**6**).

Spectrum of 8.[17] The nmr spectrum in CCl_4 solution (see Experimental Section) is consistent with an equilibrium mixture of two configurational isomers, C and D, in approximately equimolar proportion.[17] The two *tert*-octyl groups are equivalent in C and nonequivalent in D. The equivalence in C is consistent with the presence of an intramolecular hydrogen bond in which very fast tautomeric proton exchange occurs (**8a** or **8b** $\rightleftharpoons$ **8c**, Chart II). The nonequivalence in D implies the absence of such exchange. A probable structure for D appears to be **8d**, which is stabilized by two hydrogen bonds. Alternative structures with a single hydrogen bond cannot, however, be ruled out.

Rapid interconversion between different enaminoimine isomers may occur through a tautomeric diimine intermediate, which could be present in a small equilibrium concentration.

Spectrum of 7[17] **(Table I, Figure 1).** The magnetic equivalence of the *tert*-octyl groups on the terminal nitrogen atoms in **7** and an NH resonance far downfield at δ 9.98 ppm can be accounted for in either of two ways.

(1) Rapid tautomerization occurs, involving very fast proton transfer between the terminal nitrogens (**7b** $\rightleftharpoons$ **7c**, Chart II).

(2) The heavier ring atoms remain essentially stationary in intermediate positions (**7a**, Chart II).

In either case, it must be assumed that the central amino group is twisted so that its *tert*-octyl substituent remains essentially equidistant from the β-carbon atoms. In case 2, this follows directly drom the implied symmetry. In case 1, the alternative would require improbably fast oscillation of this bulky group.

The *tert*-octyl groups on the terminal nitrogens remain magnetically equivalent even at −80°, but this does not prove cyclic delocalization as in **7a.**[22]

However, the nmr spectrum of **7** strongly suggests the presence of a ring current, which is commonly accepted as a criterion for aromatic character.

Evidence for a Ring Current in 7. Aromatic ring currents give rise to shielding in two conical domes with a common truncated apex that coincides with the ring. Deshielding occurs in the remaining peripheral zone.[23]

The resonances assigned to the methylene and the *gem*-dimethyl groups in the *tert*-octyl substituent on the central (A) amino group of **7** are shifted upfield by about 0.3 ppm relative to the corresponding resonances for the equivalent *tert*-octyl groups on the terminal (B) nitrogens. (See Figure 1 and Table I.) The A amino group is forced "out of conjugation" owing to steric crowding (see above), and its *tert*-octyl substituent is therefore suspended above the plane of the ring, unlike the two *tert*-octyl substituents on the ter-

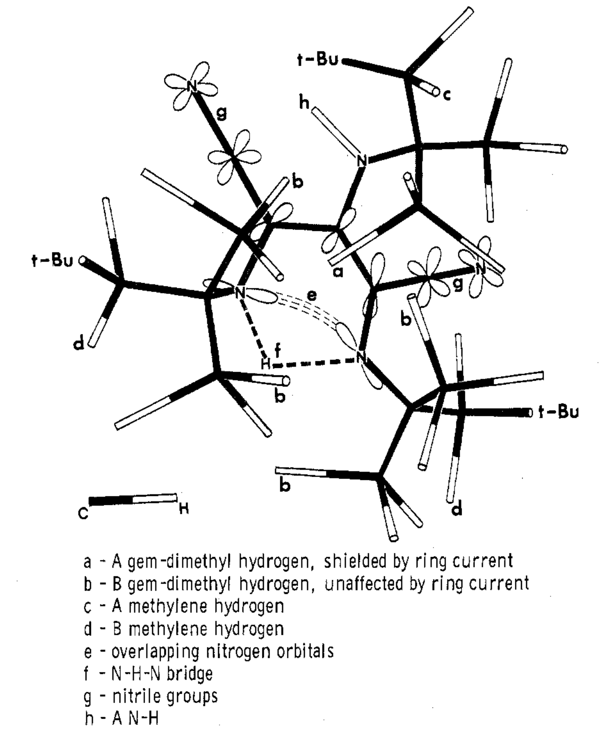
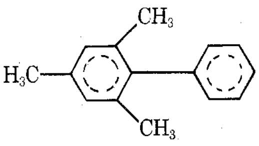


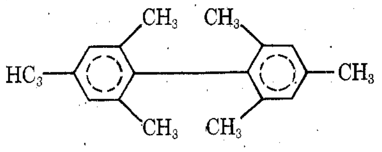
Figure 2.

minal nitrogens, which are more or less confined to that plane (Figure 2). In the A substituent, the methylene group and the two *gem*-dimethyl groups are three bond distances removed from the ring carbon atom and should thus be in the proper position to experience shielding. The magnitude of the observed shift suggests that an aromatic ring current indeed exists. Since at any one time only a single hydrogen can be located in the ring current (see Figure 2), the actual shift per affected hydrogen is greater by a statistical factor which may be as large as 8.

In phenylmesitylene and dimesityl[24] (**9** and **10** below), the *o*-methyl groups (unlike the *p*-methyl groups) are similarly suspended above and below an aromatic ring at three bond distances. Here, the difference in the shifts of the *o*-



9



10

and *p*-methyl groups is 0.30–0.45 ppm. In these compounds, both *o*-methyl groups are simultaneously located in the shielding cones. In the case of **7**, however, only one A methyl or methylene group at a time is properly oriented to experience shielding so that only an average value is recorded. Allowing for all statistical factors, the shielding observed for **7** appears to be considerably larger than that for the two aromatic model compounds **9** and **10**.

The presence of an aromatic ring current may also account for the relative shielding of the bridging proton (δ 9.88 ppm). For a strongly intramolecularly bonded N–H, this resonance is located at a surprisingly high field.[25] Relative to the corresponding N–H signal for **8**, in which the N–H–N bond is supposedly asymmetrical, the N–H signal for the N–H–N bridge in **7** is shifted downfield by only 2 ppm. Since effective homoaromatic orbital overlap requires that the bridging proton is located out of the plane of the ring (see above), it may be within one of the shielding cones associated with the aromatic ring current. (See Figure 2.)

The ultimate position of the bridge NH resonance in **7** would accordingly be determined by two opposing effects: a downfield shift associated with the symmetry of the N–H–N bridge and an upfield shift due to ring current induced shielding anisotropy.

The anomalous shielding of the proton signals in cyclopropane—with a well-established ring current—has been similarly explained.[27]

Comparison of the Vibrational Spectra of 8 and 7. The nmr evidence shows that **8** occurs in carbon tetrachloride solution as a mixture of two configurations (C and D). In the crystalline state, however, structural uniformity is suggested by the sharp melting point.[28]

Accordingly the configurational mixture in carbon tetrachloride solution shows two ir-active nitrile bands while the configurationally pure crystalline compound (KBr disk) shows a single ir-active nitrile band at 2175 cm^{-1}, which is also strongly Raman active. The Raman spectrum shows an additional band at 2222 cm^{-1}, which is ir inactive. These spectral features are consistent with a single structure with two nonequivalent nitrile groups: An enaminonitrile group (2175 cm^{-1}, strongly ir and Raman active, reported[29] range 2198–2165 cm^{-1}) and a iminonitrile group (2222 cm^{-1}, ir inactive or weakly active and Raman active, reported[30] frequency 2232 cm^{-1}).

Ir spectra of **7**, in carbon tetrachloride or in a potassium bromide disk, are essentially the same, thus pointing to identical configurations in the dissolved and crystalline states. A single ir-active band at 2220 cm^{-1} and a single Raman-active band at 2212 cm^{-1} indicate two equivalent nitrile groups which interact to give two stretching modes: one asymmetric and ir active, the other symmetric and Raman active.

The N–H Stretching Region. In this region, **8** shows several strong and medium bands consistent with the simultaneous presence of a primary and a secondary amino group.

In the same region, **7** shows a very weak split band, centered at 3360 cm^{-1}, and another very weak broad band at 3180 cm^{-1}. These bands shift to 2500 and 2300 cm^{-1} upon deuteration.

The frequency of both bands appears to be too high to be associated with the N–H–N bridge, which according to the nmr evidence (see above) is either symmetrical or exhibits very fast tautomeric proton exchange.

For compounds with demonstrated fast proton exchange in an N–H–N bridge the N–H stretch occurs at exceptionally low frequencies (*below* 3000 cm^{-1}). Examples are **1** with a broad shallow band centered at about 2850 cm^{-1}, shifting to 2260 cm^{-1} upon deuteration,[5a] and the 6-aminofulvene-2-aldimines[7] with a broad band centered at about 2625 cm^{-1}, shifting to about 2000 cm^{-1} upon deuteration.

Several additional N–H stretching modes, shifted to <3000 cm^{-1} owing to N–H–N bridge formation, have been reported.[32]

In the spectrum of **7**, there are no bands between 3000 and 1600 cm^{-1}, which are affected by deuteration, nor does deuteration give rise to an N–D band in the 2220-cm^{-1} region which would be indicative of an N–H mode submerged under the C–H absorption at ~3000 cm^{-1}.

Accordingly, the 3360- and 3180-cm^{-1} bands are best assigned to the unassociated and intermolecularly associated N–H stretching vibrations of the central amino group (reported ranges 3350–3310[33] and 3300–3150 cm^{-1} [34]).

The bridging hydrogen in **7** may give rise to a band below 3000 cm^{-1} which is so broad and shallow that it escapes detection, as is the case for protonated 1,8-bis(dimethylamino)naphthalene.[35]

The 1500–1700-cm^{-1} Region. Enaminoimines are structurally related to three classes of compounds: the amidines, the amides, and their vinylogs the enamino ketones. All three show two bands in the 1500–1700-cm^{-1} region, providing that a single hydrogen is attached to the amino nitrogen as it is in **7** or **8**. In each case the position of the shorter wavelength band is almost unchanged by deuteration. This band represents essentially the C=N or C=O stretch [ν(C=N) or ν(C=O)]. The Raman activity, expected for a double bond stretching mode, has been confirmed for the amides[36] and amidines.[37]

For the latter two classes of compounds the longer wavelength band has been assigned to a mixed vibration with a major contribution from the N–H deformation [δ(N–H)] and a minor one from the C–N stretch [ν(C–N)]. Accordingly the band is deuteration sensitive; also it has been shown to be Raman inactive.[36,37]

The extensively investigated enamino ketones[31] occur as intramolecularly hydrogen bonded s-cis forms and intermolecularly bonded s-trans forms. For these compounds the longer wavelength band (1600–1500 cm^{-1}) has been assigned to a mixed vibration of the delocalized O=C–C=C–NH system with contributions from δ(N–H) and ν(C–N) as well as ν(C=O) and ν(C=C). The deuteration sensitivity of this band is higher (~50 cm^{-1}) for the s-cis than for the s-trans forms (~15 cm^{-1}).[31]

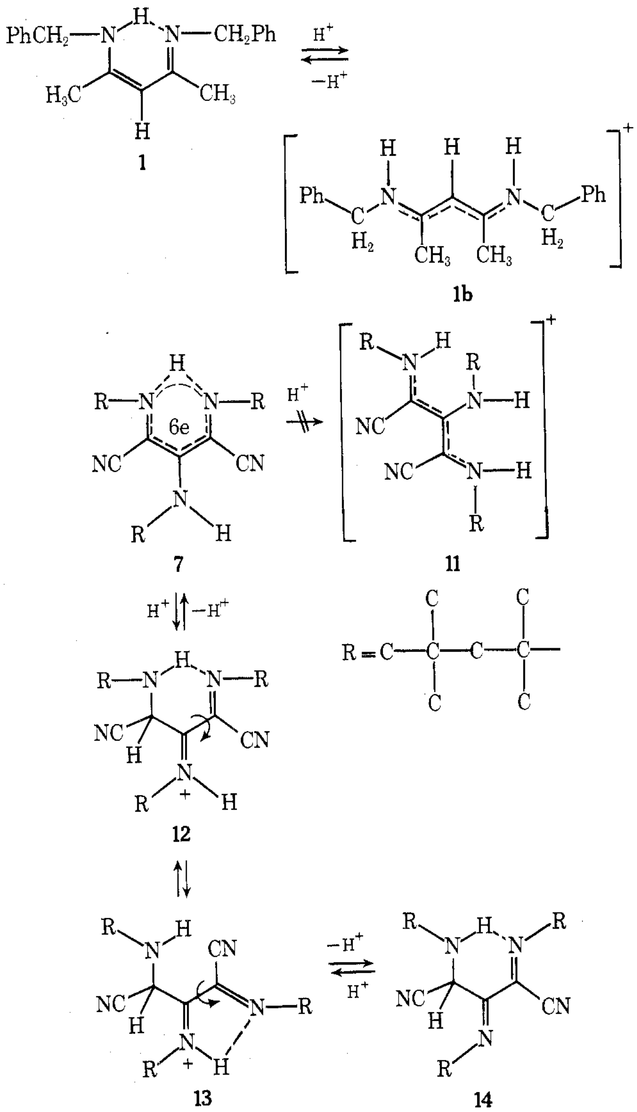
The enamino imines are the vinylogs of the amidines as well as the imino analogs of the enamino ketones. They are therefore expected to conform to the same absorption pattern in the 1500–1700-cm^{-1} region, *i.e.*, a relatively deuteration-insensitive band at higher frequency—designated AVI (amidine vinylog I)—which represents essentially ν(C=N) and a lower frequency AVII band, which is a mixed vibration with contributions from ν(C=N), ν(C=C), ν(C–N), and δ(N–H).[11b] The deuteration sensitivity of this band should be higher for the s-cis than for the s-trans forms, in analogy to the enamino ketones.

These predictions are confirmed by the spectrum of 2-amino-3-cyano-4-iminopentene-2 (**6**),[11b] which is an enamino imine with an intramolecularly hydrogen bonded s-cis configuration. Its spectrum shows an AVI band at 1617 cm^{-1} (shifted to 1600 cm^{-1} upon deuteration) and an AVII band at 1580 cm^{-1} (shifted to 1500 cm^{-1} upon deuteration).[38]

The spectrum of **8**, which is assumed to occur in a single configuration in the crystalline state (see discussion of nitrile region), is also consistent. In a KBr pellet it shows an AVI band at 1592 cm^{-1} (shifted to 1574 cm^{-1} upon deuteration) and an AVII band at 1538 cm^{-1} (shifted to 1535 cm^{-1} upon deuteration). The anomalously small isotope shift of the AVII band suggests an s-trans configuration as in **8d** (Chart II). Both AV bands of **8** are Raman active, consistent with major contributions to both from ν(C=N) and/or ν(C=C).

In this region the ir spectrum of **7**, with bands at 1578 and 1528 cm^{-1}, is superficially similar to that of **8**. However, while both bands of **8** are Raman active, only the second band is Raman active in the case of **7**. This suggests that double bond stretching modes—generally associated with strong Raman activity—make significant contributions to this band only. Upon deuteration this Raman-active band shifts from 1528 to 1472 cm^{-1},[40] indicating considerable participation of δ(N–H). This band is therefore assigned to a mixed vibration of the AVII type. The striking absence of a Raman-active, but deuteration-insensitive, AVI band—specifically assignable to δ(C=N)—may be rationalized by the cyclically delocalized structure **7a**, assuming major contributions to **7a** from **7d**-type forms, which lack the carbon–nitrogen double bond. Structure **7a** could also account for the exceptionally low frequency of the 1528-cm^{-1} band.

Chart III



Assignment of the Raman-inactive 1578-cm^{-1} band of **7** is difficult without additional data.

Ultraviolet Spectra. Uv spectra for several enaminoimines are shown in Table II.

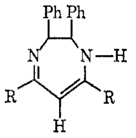
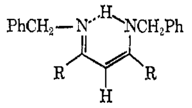
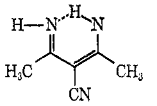
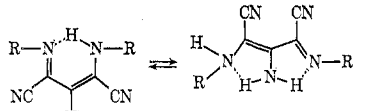
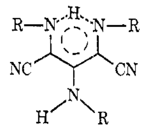
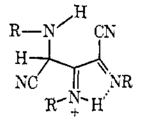
In each case protonation results in a small bathochromic shift of the long-wavelength band and a large increase in ϵ. For the well-documented case of **7**,[5b] this increase has been attributed to conversion of the s-cis free base into the vinylogous amidinium ion **1b** (Chart III) with an extended s-trans configuration.

Protonation of enaminoimines is likely to occur on the imino nitrogen, where the electron density is probably highest owing to resonance (>N–C=C–C=N– ↔ >N$^+$=C–C=C–N–$^-$). This is consistent with the reported alkylation of amidines on the double-bonded nitrogen.[41] The conjugated system is not appreciably affected by protonation on the imino nitrogen. This explains the small difference between uv max of the free base (315 nm) and of the salt (318 nm).

Ultraviolet Spectrum of 8. The uv spectrum of **8** resembles that of the other enaminoimines (Table II). The exceptionally long wavelength of the 400-nm band may be accounted for by the substituents. (An amino substituent on an unsaturated system produces shifts of 65–85 nm.)[42]

The very small wavelength changes upon protonation of **8** suggest that the chromophoric system is not appreciably affected. This is consistent with attachment of the proton

Table II
Ultraviolet Spectra of Enaminoimines and Derived Cations

Compd		Solvent	Uv max, nm	$\epsilon \times 10^{-3}$	Ref
	R = H	Tetrahydrofuran	305, 230	6.08, ~5.6	19a
	Cation	Aqueous HCl (1 *N*)	333		
	R = CH_3	Tetrahydrofuran	302, 230	6.60, ~5.6	19a
	Cation	Aqueous HCl (1 *N*)	327		
	R = H	CCl_4	318	15.0	5b
	Cation?	MeOH	282	38.0	
	R = CH_3 (1)	MeOH, MeO^-	318	17.4	5b
	Cation	MeOH	321	41.7	
 6		H_2O	292, 222	11.8, 13.2	12c
	Cation	0.001 *N* HCl	300, 222	22.0, 7.9	
 8 R = *tert*-Octyl		Isooctane	400, 234	5.59, 8.37	
		MeOH	407, 242	4.10, 7.82	
		Cation (MeOH)	410, 243	1.69, 12.64	
 7	R = *tert*-Octyl	Isooctane	416, 281, 237.5	10.09, 3.22, 8.14	
		MeOH	418, 281, 237.5	8.46, 4.72, 7.12	
		CH_3CN	418, 282, 238	9.57, 3.31, 7.83	
	Cation (13) (See Chart III)	CH_3CN, H^+	255.0	7.48	

either to the central amino group or to the imino group, as is the case for the other enamino amines. The imino group in 8 should be sufficiently basic for salt formation in spite of the electron-withdrawing nitrile substituents. In this respect 8 is probably comparable to the 1-cyanoformamidines [$R_2NC(CN){=}NH$, R = Me, Et] which form stable salts with mineral acids.[43]

Ultraviolet Spectrum of 7. In addition to long- and short-wavelength bands in approximately the same ranges as for 8, the spectrum of 7 shows a band of moderate intensity at an intermediate wavelength (281 nm, ϵ 3220, Table II), which has no counterpart in the spectra of any of the other enamino imines. A similar band, shown by cyclic amino ketones, has been attributed to transannular interaction between N and C=O.[44] There it is probably largely an excited-state phenomenon since in these substances aromatic stabilization as in 7 is impossible.

In the case of 7, however, the insensitivity of the 281-nm band to changes in solvent polarity suggests that more is involved than an excited-state phenomenon. In that case, one would expect a hypsochromic shift in more polar solvents, as occurs for $n \rightarrow \pi^*$ transitions.[45] The band at 281 nm is therefore tentatively assigned to an electronic transition of the cyclically delocalized system.

Protonation of 7. Chemical Evidence for Cyclic Delocalization. In sharp contrast to the behavior of the enaminoimine 1, which is partially protonated[5b] *even in neutral methanol*, addition of a small amount of acetic acid to solutions of 7 does not affect the spectrum. This difference is striking, although decreased basicity of 7 is expected in view of the electron-withdrawing nitrile substituents. Addition of the equivalent amount of methanesulfonic acid, however, results in protonation, as evidenced by the rapid[46] disappearance of all three bands, characteristic of the free base (Table II).

The originally yellow solution becomes at first brownish red, and the spectrum (CH_3CN) of the protonated species consist of two new bands, uv max 247 nm (ϵ 16,000) and 510 (1780). During the next few minutes, the intensity of the bands at 247 and 510 nm diminishes rapidly, and the solution becomes colorless. Simultaneously, a new band emerges, uv max 255 nm (ϵ 7944).

The disappearance of both long-wavelength bands of the free base (418.0 and 282 nm) suggests shortening of the chromophoric system which can be accounted for by protonation on carbon. Accordingly, it is proposed that the initial band at 247 nm is due to the s-trans immonium ion 12 (Chart III). The subsequent shift of the 247-nm band to 255 nm is associated with a decrease in ϵ_{max}. Since such a decrease is indicative of a trans–cis isomerization,[5b] the 255-nm band is assigned to the s-cis ion 13.[47] Examination of the products supports these assumptions.

From the solution of protonated 7 the salt 13 CH_3SO_3H was isolated; it had uv max (MeOH) 255 nm (ϵ 7480). Treatment of this salt with base gave the conjugated diimine 14.

In the presence of a catalytic amount of acetic acid, 14 reverts quantitatively to 7.

The structures assigned to 13 and 14 are based on elemental analysis and spectral data. (See Experimental Section)[49]

The immonium ion 13, resulting from protonation on carbon, appears to be the thermodynamically determined product of protonation of 7, which itself is the most stable species under essentially neutral conditions.

The anomalous protonation behavior of 7 argues against the classical enamino imine structure **7b**. In accordance with the protonation of 8 (see above) this structure is expected to protonate on the imino nitrogen (to give **11**, Chart III) or on the central amino group, but not on carbon.

The central amino group is the more likely site, since it should be more basic than the corresponding group in **8**. In **7b** the additional *tert*-octyl substituent should twist the electron pair on nitrogen out of conjugation with the ring and with the β-nitrile group. This should result in diminished electron withdrawal.

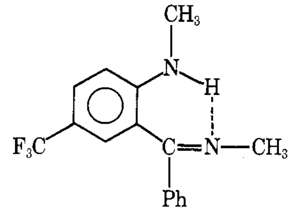
In either case structure **7b** fails to account for the striking changes observed upon protonation of **7**. The wavelength changes due to protonation of **7b** are expected to be minor, as is the case for 8 and the other enaminoimines (Table II).

Protonation of 7 on carbon in preference to the three available sites on nitrogen becomes understandable if 7 has the alternative homoheteroaromatic structure **7a.** This structure implies transfer of electron density from the terminal nitrogens to the α-carbon atoms and the nitrile nitrogens. Accordingly, kinetically controlled protonation on these carbon atoms becomes a possibility. This is not without precedent and actually may be the rule for five-membered hetero(N) aromatics, since protonation of alkylpyrroles has been reported to occur exclusively on the carbon atoms α to nitrogen.[52]

Alternatively, initial protonation of **7a** may occur on a nitrile nitrogen or on the central amino group. In both cases, the ion 12 could result from a fast subsequent proton shift.[53] Protonation of the central amino group may occur without disturbing the homoaromatic ring if it is twisted out of conjugation with the π system. The driving force for the subsequent proton shift could be provided by high electron density on the β-carbon atoms.

A single instance was found in the literature of a neutral heterocyclic system for which spectral anomalies suggest possible homoaromaticity similar to **7a.**

The atypical enaminoimine structure in **15** is fused to an aromatic ring and occurs in an anti (phenyl) configuration [ν(NH) 3570 cm^{-1}] and in an intramolecularly hydrogen bonded syn (phenyl) configuration [ν(NH) 3010 cm^{-1}].[54]



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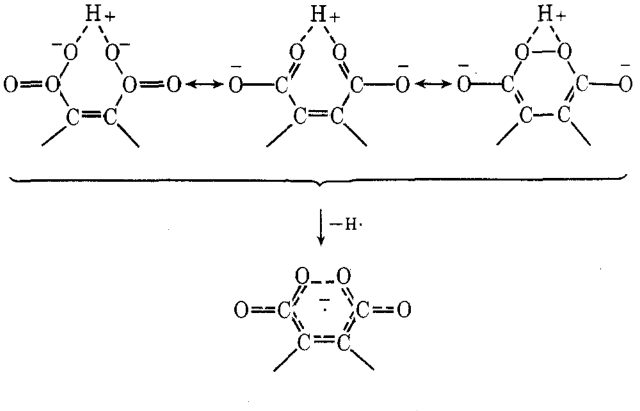
The syn isomer has uv max 240 nm (ϵ 30,700), 273–278 (8200), and 358 (6500). The anti isomer has uv max 256 nm (ϵ 24,300). The authors ascribe the anomalous spectrum of the syn form to "expansion of the conjugated system through hydrogen bridge formation."

Clear implications for a broader family of compounds do not yet exist. Cyclic delocalization may be contingent upon stringent structural requirements. As an example a classical structure is indicated for 8 in spite of its close similarity to **7**.

Cyclic delocalization may, however, occur in some structures shown to have symmetrical intramolecular hydrogen bridges which characteristically are anomalously strong and short. Possible examples are the monoanions of maleic[56a] and phthalic acid[56b] and the biochemically important dianion of *cis*-aconitic acid.[56c] The acid maleate anion has, in the crystalline state, C_s rather than C_{2v} symmetry,[56d] suggesting an O–H–O bridge that is bent out of the plane[57] and may allow the necessary overlap of the p orbitals on oxygen.

Upon X-ray irradiation of the crystal, this ion loses the bridging hydrogen with formation of an extremely stable symmetrical anion radical, for which a cyclically delocalized semiquinone-type structure has been proposed,[58] *e.g.*



Experimental Section

Equipment. The following instruments were used: a Perkin-Elmer 621 double beam grating ir spectrometer, a Laser-Raman Carey 91 spectrometer, and a Varian HA-100 nmr spectrometer.

Materials. The preparation and physical properties of 1,2-di-*tert*-octylamino-3-*tert*-octylimino-1,3-dicyanopropene-1 (7) and of 1-*tert*-octylamino-2-amino-3-*tert*-octylimino-1,3-dicyanopropene-1 (8) are presented in ref 17. The nmr data of 8 are repeated below, since they are relevant to the above discussion, but are not tabulated.

Nmr Spectrum of 8. Nmr (CCl_4) δ 1.017 [2 $C(CH_3)_3$ of C + $C(CH_3)_3$ of D],[59] 1.100 [$C(CH_3)_3$ of D], total 18 H; 1.386 [$C(CH_3)_2$ of D], 1.474 [2 ($CC(CH_3)_2$ of C], 1.586 [$C(CH_3)_2$ of D], total 12 H; 1.693 (CH_2 of D), 1.860 (2 CH_2 of C), 1.920 (CH_2 of D), total 4 H; 3.636, 4.800, 7.650 ppm (NH_2 of C + D and NH of C + D), total 3 H.

Methanesulfonic Acid Salt of 7 (13). To a solution of 0.25 g (5.2×10^{-4} mol) of **7** in 5 ml of ether was added a solution of 0.05 g (5.2×10^{-4} mol) of methanesulfonic acid in 5 ml of ether. After 1 hr at −10°, a crystalline precipitate had formed. The crystals were collected by filtration and redissolved in 1 ml of chloroform, and ether was added dropwise until incipient crystallization occurred. After 1 hr at −10°, filtration gave 0.18 g of the methanesulfonic acid salt: mp 118.5–120° dec; uv max (MeOH) 255 nm (log ϵ 3.87); nmr ($CDCl_3$) δ 0.97, 1.02, 1.07 [27 H total, 3 $C(CH_3)_3$]; 1.60 w, 1.67 s, 1.93 w, 2.03 s [two unresolved multiplets, 24 H total, 3 CH_2 + 3 $C(CH_3)_2$]; 2.40 (1 H, NH); 2.74 (3 H, $CH_3SO_3^-$); 5.83 (1 H, CH); 8.00 ppm (1 H, NH).

Anal. Calcd for $C_{30}H_{57}N_5SO_3$: C, 63.44; H, 10.14; N, 12.33; S, 5.64. Found: C, 63.01; H, 10.39; N, 12.26; S, 5.25.

1-*tert*-Octylamino-2,3-di-*tert*-octylimino-1,3-dicyanopropane (14). A 5-g quantity of **13** was dispersed in 30 ml of ether and shaken with cold 25% aqueous KOH. The solid disappeared, and the ether layer became light yellow. The aqueous layer was discarded, the ether layer was dried over magnesium sulfate, and the ether was evaporated *in vacuo*. The residue was twice recrystallized from warm (50°) hexane: yield 3.2 g of almost colorlees crystals of **14;** mp 91.5–93°; uv max (isooctane) 216.0, 247.5, 316.7 nm (log ϵ 4.05, 3.88, 1.73); ir ($CHCl_3$) 3230 w (NH), 2180, 2215 vw ($C{\equiv}N$), 1685 w, 1645 s ($N{=}C{-}C{=}N$); nmr ($CDCl_3$) 0.90 [18 H, 2 $C(CH_3)_3$], 1.22, 1.37, and 3.10, 3.25 [2 H (heterosteric), CH_2], 1.73, 1.66 [2 H (heterosteric), CH_2], 1.42, 1.48, 1.51 (double area), 1.57, 1.60 [18 H, six heterosteric CH_3, 3 $C(CH_3)_2$], 5.01 [1 H, CH], 7.64 ppm [1 H, NH, disappears upon deuteration]; mass spectrum (70 eV) *m/e* 471 (M^+); mol wt 469 (Thermonam).

Anal. Calcd for $C_{29}H_{53}N_5$: C, 73.70; H, 11.33; N, 14.95. Found: C, 73.37; H, 11.49; N, 14.96.

Rearrangement of 14 to Give 7. A 4.0-g quantity of **14** was dissolved in 2 ml of ether. Upon addition of 0.5 ml of acetic acid, the light-yellow solution became deep orange. After 1 hr at room temperature, the solvents were evaporated *in vacuo*.

The residue was purified by three crystallizations from pentane at −30°, using decolorizing carbon the first time: yield 2.8 g of **7,** identified by ir spectrum and mixture melting point determination.

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Registry No.—**7**, 40127-68-2; **8**, 40127-66-0; **13**, 51934-35-1; **14**, 51934-36-2.

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