

Structural Effects on Nitrile Infrared Integrated Intensities of Alpha,Beta-Diaryl Cyanoethylenes: Hammett and Quantum Chemical Approaches

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The nitrile infrared intensities of a series of α,β -diaryl cyanoethylenes were juxtaposed to the associated substituent constants, HMO and SCF-MO indices and fair to excellent correlations were established. The competitive resonance of the nitrile group with alpha- and beta-aryl substituents is discussed. HMO calculations were used to estimate the steric hindrance to conjugation caused by polycyclic substituents and SCF-MO calculations were made to obtain uniform predictions of nitrile intensities and frequencies for heterocyclic derivatives of acrylonitrile.

Introduction

The integrated intensities of nitrile infrared absorption bands are usually more sensitive to structural changes than the associated vibrational frequencies [1]. Thus, a study of the structural effects on these intensities would be of substantial interest for the organic structural analysis.

A considerable number of correlations of infrared frequencies and intensities with Hammett type reactivity constants has been reviewed in the literature (see [1, 2] and references therein). The LFE type relationships for nitrile frequencies ν_{CN} and integrated intensities A_{CN} were extensively studied in the cases of substituted benzonitriles [1, 4-7] and other conjugated nitriles [1, 8, 9]. Satisfactory and excellent correlations have been obtained with the electrophilic substituent constants σ^+ [1-9]. Brown has demonstrated [10] that in the studies of integrated intensities the substituent constants should be related to the quantity $A^{1/2}$, but not to A or $\log A$.

The capability of the simple Hückel molecular orbital (HMO) method to predict semiquantitatively the magnitude of A_{CN} with the aid of a simplified model of the nitrile vibration has been shown recently [11]. Satisfactory correlations of $A_{CN}^{1/2}$ and the change of calculated dipole moment $\Delta\mu$ during this vibration were found for several types of conjugated nitriles [11]. Some of these studies were combined with interpretations of the relationships between ν_{CN} and the calculated bond order P_{CN} [9].

The aim of the present paper is to compare the scope and the quality of correlations given by the LFE and quantum chemical approaches to the study of structural effects on A_{CN} and ν_{CN} for a series of closely similar nitriles. This restriction is necessary because of the different slopes of the correlations for the different structural classes of conjugated nitriles [11]. Substituted α,β -Diaryl acrylonitriles of general formula



are suitable for the purpose of this work. These conjugated systems provide the possibility to investigate thoroughly the substituent effects as functions of the type and position (*o*, *m*, *p*- in both α - and β -phenyl rings of substituted cyanostilbenes) as well as the effects of certain polycyclic and heterocyclic substituents.

Results and Discussion

The integrated intensities of nitrile absorption bands of the studied series of *trans*- α,β -diaryl acrylonitriles (infrared spectra recorded in CHCl_3) are summarized in Table I. The effects of substituents in the alpha-aryl fragment are represented by compounds 1-10, 30, 31. A_{CN} for these molecules can be found in the relatively small range of 2.4 to $3.61 \cdot \text{mol}^{-1} \cdot \text{cm}^{-2}$. Donor substituents to the α -phenyl ring as well as polycyclic alpha-aryls cause enhancement of nitrile intensities. A_{CN} however is independent, within the experimental error, on the position of the substituents (*m*- or *p*-) to the α -phenyl ring. The same substituent effects on the nitrile frequencies can be observed in Table I. All these

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Table I. Infrared and Hückel MO data for α,β -diaryl-acrylonitriles

No.	Ar _α	Ar _β	10 ⁻³ ·A _{CK}	A _{CK} ^{1/2}	Δμ	ν _{CK}	ρ _{CK}
1	Phenyl	Phenyl	2.6	51.0	0.756	2218.0	0.9199
2	Phenyl	4-Methylphenyl	2.7	52.0	0.758	2217.5	0.9200
3	Phenyl	4-Methoxyphenyl	2.8	53.0	0.758	2217.5	0.9202
4	Phenyl	3-Methoxyphenyl	2.8	53.0	0.757	2219.0	0.9199
5	Phenyl	4-Aminophenyl	3.3	57.5	0.755	2217.5	0.9206
6	Phenyl	4-Dimethylaminophenyl	3.3	57.5	0.763	2217.5	0.9210
7	Phenyl	4-Fluorophenyl	2.6	51.0	0.757	2218.5	0.9199
8	Phenyl	4-Nitrophenyl	2.4	49.0	0.748	2220.5	0.9197
9	Phenyl	3-Nitrophenyl	2.55	50.5	0.751	2219.0	0.9188
10	Phenyl	2-Naphthyl	2.7	52.0	0.760	2219.5	0.9200
11	4-Methylphenyl	Phenyl	3.3	57.5	0.786	2217.0	0.9189
12	3-Methylphenyl	Phenyl	2.6	51.0	0.754	2216.5	0.9199
13	4-Methoxyphenyl	Phenyl	4.4	66.5	0.815	2215.0	0.9178
14	3-Methoxyphenyl	Phenyl	2.6	51.0	0.755	2217.0	0.9199
15	4-Aminophenyl	Phenyl	6.0	77.5	0.921	2211.0	0.9158
16	3-Aminophenyl	Phenyl	3.2	56.5	0.752	2217.0	0.9200
17	4-Dimethylaminophenyl	Phenyl	8.1	90.0	1.005	2207.5	0.9136
18	3-Fluorophenyl	Phenyl	2.15	46.5	0.756	2218.5	0.9199
19	4-Chlorophenyl	Phenyl	2.4	49.0	0.739	2218.0	0.9203
20	3-Chlorophenyl	Phenyl	2.1	46.0	0.757	2219.5	0.9199
21	4-Nitrophenyl	Phenyl	1.7	41.0	0.700	2220.5	0.9214
22	3-Nitrophenyl	Phenyl	1.6	40.0	0.714	2220.0	0.9210
23	4-Biphenyl	Phenyl	3.3	57.5	0.795	2217.5	0.9193
24	2-Naphthyl	Phenyl	3.5	59.0	0.843	2216.0	0.9194
25	4-Dimethylaminophenyl	4-Nitrophenyl	7.6	87.0	0.986	2209.5	0.9135
26	4-Pyridyl	Phenyl	1.4	37.5	0.683	2222.0	0.9219
27	3-Pyridyl	Phenyl	2.0	44.5	0.751	2219.5	0.9188
28	2-Furyl	Phenyl	3.55	59.5	0.841	2216.5	0.9180
29	2-Thienyl	Phenyl	3.3	56.5	0.918	2214.0	0.9150
30	Phenyl	1-Naphthyl (0°)	3.2	56.5	0.744	2213.0	0.9207
		(30°)			0.738		0.9189
		(45°)			0.770		0.9170
		(60°)			0.786		0.9149
		(75°)			0.797		0.9133
31	Phenyl	1-Phenyl (0°)	3.6	60.0	0.722	2213.5	0.9211
		(45°)			0.761		0.9172
		(60°)			0.781		0.9150
32	1-Naphthyl (0°)	Phenyl	2.7	52.0	0.829	2219.0	0.9181
	(30°)				0.772		0.9201
	(40°)				0.736		0.9215
33	9-Anthryl (0°)	Phenyl	1.7	41.0	0.974	2224.5	0.9153
	(45°)				0.756		0.9207
	(60°)				0.694		0.9237
34	9-Phenanthryl (0°)	Phenyl	2.5	50.0	0.738	2219.5	0.9181
	(40°)				0.688		0.9215
35	1-Pyrenyl (0°)	Phenyl	4.5	67.0	1.10	2216.5	0.9171
	(35°)				0.919		0.9200
	(45°)				0.827		0.9217
36	1-Naphthyl (0°)	1-Naphthyl (0°)	2.8	53.0	0.815	2221.0	0.9191
	(40°)	(60°)			0.764		0.9169
	(60°)	(40°)			0.682		0.9226

results can be explained by the absence of direct resonance of alpha substituents with the indicator nitrile group, that is, the mechanism of the transmission of these effects is inductive, at first, and then competitive conjugation with regard to the effects transmitted through the ethylenic double bond.

We attempted to relate A_{CK} and ν_{CK} of compounds 1-10 to σ_r, σ^o, σ, σ⁻ and σ⁺ substituent constants, and obtained correlation coefficients in the range 0.52-0.88. This result indicates that no individual mechanism of transmission of substituent effects dominates in our case. A second reason for the low correlation coefficients is the large relative error of

ν_{CN} measurements and the small variance of ν_{CN} values for the α -substituted cyanostilbenes.

The nitrile intensities of β -substituted cyanostilbenes can be found in the range 1.4–8.1 l·mol⁻¹·cm⁻², that is, four times larger range than that for α -substituted compounds. The effects of 4'- β -substituents are the strongest obviously because of the possibility for direct resonance of these substituents with the nitrile group. As known, nitrile intensities of conjugated nitriles fit statistically better to the σ^+ -constants than to σ [1–5, 8, 9] indicating that the nitrile group is a strong resonance acceptor. The results for α -phenyl- β -aryl acryloethylenes obey the same rule – the correlation coefficient for $\nu_{CN}^{1/2} \cdot \sigma^+$ is 0.985 whereas for $\nu_{CN}^{1/2} \cdot \sigma$ is 0.916. This is an evidence for the dominating role of direct resonance of β -substituents with the nitrile group in the studied substituent effects.

The slope of the correlation $\nu_{CN}^{1/2} \cdot \sigma^+$, –19.34, for α, β -diaryl acryloethylenes is very close to that found for arylidene-cyanoacetates (18.97, *trans* with respect to the ethoxycarbonyl group), but is considerably lower than the value found for *trans*-cinnamionitriles, –32.30 [1, 9]. The spatial extension of the conjugated system in the latter case gives rise to larger changes of the dipole moment during the nitrile vibration (i.e. one can assume larger dipole moment derivative $\partial \mu / \partial Q$) and respectively a larger sensitivity to substituent effects [9].

The integrated intensities ν_{CN} of several α -phenyl- β -hetero substituted acrylonitriles (compounds 26–29 in Table I) obey the relationship $\nu_{CN}^{1/2} \cdot \sigma^+$ on use of the following values for the respective σ^+ -constants: 4-pyridyl, 0.87; 3-pyridyl, 0.30 [14]; 2-furyl, –0.55; 2-thienyl, –0.16 [15]. We must note, however, that the different methods used for determination of σ^+ -constants for these "substituted benzenes" give very different values [16, 17] and there is no persuasive justification of the use of any of these at present. Consider for example the ν_{CN} and ν_{CN} data for benzonitrile (2232.2 and 28.7), 2-cyanofuran (2236.3 and 31.9) and 2-cyanothiophene (2225.7 and 28.7) in CCl₄ [16] and for compounds 1 and 26–29 in Table I together with the following correlation equations:

$$\nu_{CN} = 2232.9 + 7.00 \sigma^+ \quad (1)$$

for benzonitriles [5, 7] (solvent CCl₄),

$$\nu_{CN}^{1/2} = 29.6 - 19.0 \sigma^+ \quad (2)$$

for benzonitriles [16] (solvent CCl₄),

$$\nu_{CN} = 2217.4 + 4.95 \sigma^+ \quad (3)$$

for α -phenyl- β -aryl acrylonitriles (in CHCl₃),

$$\nu_{CN}^{1/2} = 52.8 - 19.34 \sigma^+ \quad (4)$$

for α -phenyl- β -aryl acrylonitriles (in CHCl₃).

Substituting the values of ν_{CN} and $\nu_{CN}^{1/2}$ in the above relationships one obtains the following "substituent" constants for the considered heterocycles:

	2-Furyl	2-Thienyl	4-Pyridyl ^a	3-Pyridyl ^a
eq. (1)	0.49 ± 0.05	-1.0 ± 0.1		
eq. (2) [13]	-0.13	-0.44		
eq. (3)	-0.2 ± 0.1	-0.7 ± 0.2	0.9 ± 0.2	0.4 ± 0.1
eq. (4)	-0.35 ± 0.1	-0.2 ± 0.1	0.8 ± 0.2	0.4 ± 0.1

^a The "substituent" constants for 4-pyridyl and 3-pyridyl moieties determined by chemical reactivity measurements lie between the values 0.86–0.87 and 0.30–0.78 respectively [14].

It is evident that the σ^+ "substituent" constant in the pyridine series are qualitatively consistent with both infrared spectral data and chemical reactivity results. In contrast to this, the results for 2-furyl and 2-thienyl are contradictory even in the framework of the considered spectral data.

The correlation $\nu_{CN} \cdot \sigma^+$ for α -phenyl- β -aryl acrylonitriles, in general, is satisfactory (Table II, ser. 1). The frequencies of 2-furyl and 2-thienyl substituted compounds however deviate significantly and were

Tab. II. Correlations of nitrile frequencies and intensities of 1,2-diaryl-cyanoethylenes and some structural parameters.

No.	Series	Relation-ship	ρ	R	S	n
1		ν_{CN}/σ^+	4.95	0.973	0.83	17
2		$\nu_{CN}^{1/2}/\sigma^+$	-19.34	0.985	2.31	19
3		$\nu_{CN}^{1/2}/\sigma$	-30.03	0.916	4.95	19
4		$\nu_{CN}^{1/2}/\nu_{CN}$	-3.01	0.893	5.19	36
5		ν_{CN}/ρ_{CN}	1670	0.966	0.935	17
6		$\nu_{CN}^{1/2}/\Delta \mu$	371.2	0.622	2.69	10
7		$\nu_{CN}^{1/2}/\Delta \mu$	163.0	0.974	3.57	18

σ = slopes of the relationships,

R = correlation coefficients,

S = mean deviations,

n = number of data points.

excluded from the statistical treatment. The attempt to correlate $A_{CN}^{1/2}$ and ν_{CN} for the entire series of compounds (Table II, ser. 4) yielded nothing more than a rough relationship ($r=0.893$; significant deviations were observed for compounds 22, 25, 29, 30, 31, 33, 35, 36, that is, strongly conjugated stilbenes, heterocyclic derivatives and compounds having probably non-planar structure).

We conclude that the Hammett approach is satisfactory for interpretations of nitrile frequencies and integrated intensities for the α -phenyl- β -aryl acrylonitrile series. This approach, however, is inefficient in the cases of α -aryl- β -phenyl acrylonitriles and for acrylonitriles substituted by a five-membered heterocycle in the β -position. The $\rho\sigma$ relationships are not applicable for acrylonitriles with polycyclic substituents, too.

Quantum Chemical Approach

The integrated intensity of a given normal vibration, as known [18], is a function of the dipole moment derivative with respect to the corresponding normal coordinate,

$$\frac{\partial \mu}{\partial Q_k} = \sum_j (\frac{\partial \mu}{\partial R_j})(\frac{\partial R_j}{\partial Q_k}) = \sum (\frac{\partial \mu}{\partial R_j}) \cdot L_{kj}$$

where R is the normal coordinate and L is the transformation matrix for the internal coordinates Q to R. By virtue of the fact that the nitrile vibration

is practically localized in the C-C≡N fragment the required dipole moment derivative $\partial \mu / \partial Q_{CN}$ can be successfully substituted [11] by the change of dipole moment on changes of nitrile configurations involving these three atoms only. The experimental integrated intensity is proportional to the square of the transition moment of the given vibration [18] and, therefore

$$A \sim (\Delta \mu / \Delta R)^2 \text{ or } A^{1/2} \sim \Delta \mu / \Delta R.$$

The geometry of the studied α, β -diaryl acrylonitriles was taken from crystallographic data [20] with equilibrium bond lengths C-C(N) — 1.4675 Å, and C≡N — 1.16 Å. In the largest phase of the studied nitrile vibration the C-C bond was shortened by 0.046 Å, whereas the C≡N bond was taken longer by 0.065 Å [11]. The required changes of dipole moments were calculated by use of the simple Hückel method with parameters $K_{CC}=0.9$, resp. 1.074 β , $K_{CN}=1.4$, resp. 1.234 β and $h_N=0.5 \beta$ [11] and standard values for aryl substituents [21]. Pi-electron SCF-MO (PPP) calculations for several molecules were made using a set of statistically fitted parameters [22] within the traditional "tight binding" scheme, and the following β_{CN}^{core} parameters for the C-C≡N fragment were employed: $\beta_{CN}^{core} = -2.15/-2.15 \text{ eV}$ and $\beta_{CN}^{core} = -2.65/-2.5 \text{ eV}$ for the equilibrium and largest-phase-configurations respectively.

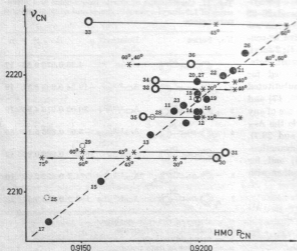


Fig. 1. Plot of nitrile frequencies of the studied α, β -diaryl acrylonitriles vs. the calculated HMO bond orders P_{CN} . Light circles represent the models of the sterically hindered molecules; broken circles — the heterocyclic derivatives. For the numbering see Table I.

The Hückel results are juxtaposed with the experimental integrated intensities in Table I and on Figs. 1 and 2. The results of the statistical treatment are given in Table II. The subdivision of the studied series of compounds in smaller parts in order to elucidate the mechanism of the interaction of the nitrile group and aryl substituents (statistical results in Table II) indicates that HMO does not predict correctly the substituent effects of α -aryls because of its capability to account only for direct resonance interactions. Nevertheless, the calculated $\Delta\mu$ for α -aryl- β -phenyl cyanoethylenes correspond qualitatively to the measured $A_{CN}^{1/2}$. This is not a result of the changes of inductive effects represented by the corresponding HMO parameters, but is probably due to the commensurability of inductive and the actual substituent effects which can not be transmitted through the favoured by HMO calculations direct resonance mechanism. The same is valid for the calculated HMO bond orders P_{CN} , which are practically identical for all α -aryl- β -phenyl cyanoethylenes (Table I, see also [13]).

As mentioned above, the LFE relationships are of no use in the interpretation of the studied spectral properties of acrylonitriles with five-membered heterocyclic substituents. HMO calculations, however, give incorrect (even qualitatively) predictions of A_{CN} of these compounds, too. Comparative HMO calculations for benzonitrile, 2-cyano-furan and 2-cyano-thiophene (Table III) gave bond orders P_{CN} and dipole moment changes $\Delta\mu$ qualitatively consistent with the experimental data. This is not the case, however, for α -phenyl- β -hetero-substituted acrylonitriles. The attempt to reproduce the course of variation of experimental nitrile intensities by variation of sulphur and oxygen parameters in a

wide range of values gave a negative result. One might suppose that the HMO method is incapable to reproduce the larger polarisability of sulphur orbitals by any combination of coulombic and resonance parameters. Proper predictions of infrared frequencies and intensities require, therefore, the use of quantum chemical methods which guarantee a more adequate description of the electronic structure. Such a method would facilitate the elucidation of the nature of substituent effects in the studied molecules, too.

Table III embraces the experimental data for some of the studied diaryl cyanoethylenes and the results of HMO and SCF-MO pi-electronic calculations. One should note that the latter reproduce correctly the observed changes of nitrile frequencies and intensities of both β -hetero-substituted and α -aryl- β -phenyl acrylonitriles, Fig. 3. The result for β -3'-indolyl derivative is also qualitatively consistent with the low experimental frequency ν_{CN} and intensity A_{CN} . The quantitative deviations in this case should be considered as a result of the steric hindrance to conjugation caused by the bulky 3'-indolyl moiety.

The results of the above SCF-MO calculations suggest that substituent effects of α -aryl fragments are transmitted to the nitrile group through a resonance mechanism competitive to the conjugation through the ethylenic bond. The failure of LFE considerations in this case should be attributed, therefore, to the insufficient precision of the method as well.

As known, both infrared frequencies and intensities of conjugated molecules are sensitive to steric hindrance to conjugation. The quantum chemical approach provides the possibility to estimate the

Table III. Infrared, HMO and PPP MO data.

No.	Compound	ν_{CN}	$A_{CN}^{1/2}$	HMO P_{CN}	HMO $\Delta\mu$	PPP P_{CN}	PPP $\Delta\mu$
	Benzonitrile ^a	2232.2	28.7	0.9270	0.837	0.9289	0.1449
	2-Cyanofuran ^a	2236.3	31.9	0.9197	0.867	0.9232	0.1572
	2-Cyanothiophene ^a	2225.7	37.8	0.9153	1.007	0.9211	0.1661
1	1,2-Diphenyl-acrylonitrile ^b	2218.0	51.0	0.9199	0.869	0.9221	0.1304
5	1-(4-Aminophenyl)-2-phenyl-acrylonitrile ^b	2217.5	57.5	0.9206	0.869	0.9219	0.1556
8	1-(4-Nitrophenyl)-2-phenyl-acrylonitrile ^b	2220.5	49.0	0.9197	0.865	0.9236	0.1253
19	1-Phenyl-2-(4-chlorophenyl)-acrylonitrile ^b	2218.0	49.0	0.9203	0.739	0.9213	0.1318
28	1-Phenyl-2-(2-furyl)-acrylonitrile ^b	2216.5	59.5	0.9180	0.841	0.9065	0.1533
29	1-Phenyl-2-(2-thienyl)-acrylonitrile ^b	2214.0	56.5	0.9150	0.902	0.9177	0.1513
34	1-Phenyl-2-(9-phenanthryl)-acrylonitrile ^b	2219.5	50.0	0.9181	0.738	0.9193	0.1240
37	1-Phenyl-2-(3-indolyl)-acrylonitrile ^b	2209.5	46.0	-	-	0.9179	0.1400

^a In carbon tetrachloride; ^b in chloroform.

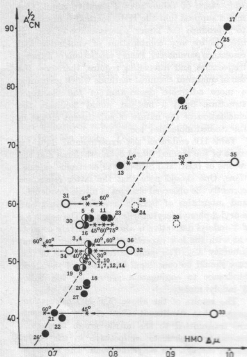


Fig. 2. Plot of nitrile intensities of the studied α,β -diaryl acrylonitriles $A_{CN}^{1/2}$ vs. the calculated dipole moment changes $\Delta\mu$ by the HMO method. Light circles represent the models of sterically hindered molecules; semi-light circles - the models of α -aryl- β -phenyl acrylonitriles; broken circles - the models of heterocyclic derivatives. For the numbering see Tables I and IV.

dihedral angle between the planes of two pielectronic molecular fragments connected by a "single" bond. HMO calculations, for example, were used jointly with carbonyl, $\nu_{C=O}$ and nitrile frequencies and polarographic half-wave potentials, and yielded plausible values for the angles of twist of α,β -diaryl acrylonitriles [12, 23] and aryl-methylene-1,3-indandiones [24]. The rotation of the studied bulky aryl substituents around the "single" C-C bond was simulated by variation of the resonance parameter of this bond [12, 23-25]. The estimates of rotation angles found for diaryl cyanoethylenes in this work are generally consistent with

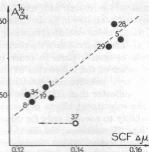


Fig. 3. Plot of $A_{CN}^{1/2}$ of several α,β -diaryl acrylonitriles vs. the calculated PPP-MO dipole moment changes $\Delta\mu$. For the numbering see Tables I and III.

these found by the polarographic method [23]. One should note that the values of $\Delta\mu$ for aryl substituents in the β -position decrease on rotation whereas these for α -substituents increase. The effect of rotation on nitrile bond orders is reversed, but again different for α - and β -substituents. The fact that the rotation gives rise to different directions of the changes of $\Delta\mu$ and ν_{CN} for the different positions of aryl substituents can be considered as an additional evidence for the competitive resonance of the latter and the indicator nitrile group.

Table IV. Angles between the planes of the double bond and of polycyclic substituents estimated from the correlations for $A_{CN}^{1/2}$, ν_{CN} , and $E_{1/2}$.

No.	Polycyclic substituent	ν_{CN}	$A_{CN}^{1/2}$	$E_{1/2}$ [23]
30	alpha-(1-Naphthyl)	45°	67°	55°
31	alpha-(1-Pyrenyl)	44°		
32	beta-(1-Naphthyl)	34°	32°	37°
33	beta-(9-Anthryl)	61°	59°	62°
34	beta-(9-Phenanthryl)	36°		37°
35	beta-(1-Pyrenyl)	29°	42°	45°
36	alpha-(1-Naphthyl)		60°	
	beta-(1-Naphthyl)		40°	

The errors of the given estimates, making provision for the mean deviations of the correlations for A_{CN} and ν_{CN} , are not less than 3° for the beta-aryl substituents and substantially larger for the alpha-substituents. In the latter case, in addition, the estimates from ν_{CN} should be considered as lower and these from A_{CN} as upper threshold values, since the rotation of the alpha-aromatic substituents is accompanied by a smooth change of the class of the corresponding nitrile. This problem is discussed in more details in [12].

Experimental

The studied α,β -diaryl cyanoethylenes were synthesized as described previously [12, 13, 26]. The spectra were recorded by an UR-20 Zeiss spectrophotometer calibrated by the gas spectra of DCI [27]

and NH_3 . 0.05–0.20 M chloroform solutions in NaCl cells of path length 0.4 and 1 mm were used. The integrated intensities were calculated according to Ramsey [29] and the estimated experimental errors were 0.5 cm^{-1} for the frequencies and 10% for the intensities.

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