ELSEVIER

Journal of Molecular Structure 344 (1995) 205-215

Journal of
MOLECULAR
STRUCTURE

# Infrared spectra and structure of phenylacetonitrile and of its carbanion: an ab initio force field treatment

I.G. Binev*, J.A. Tsenov, E.A. Velcheva, I.N. Juchnovski

*Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Received 16 August 1994

## Abstract

The structures of phenylacetonitrile and of its carbanion have been studied on the basis of IR spectroscopic data (including literature results) and of ab initio force field calculations. The assignment (D. Croisat et al., J. Org. Chem., 157 (1992) 6435) of the IR bands of phenylacetonitrile, its $d_5$ analogue, and their carbanions has been confirmed. An excellent linear correlation ($R = 0.999$) has been found between the theoretical and experimental IR frequencies of the species studied. The calculations predict well the strong increase in intensity (five to 42 fold) of the $\nu_{CN}$, $\nu_{S8}$ and $\nu_{19}$ bands which accompanies the conversion of the phenylacetonitrile molecule to its carbanion. The structures of both sodium and potassium derivatives of phenylacetonitrile in dimethyl sulfoxide are close to that of the kinetically free phenylacetonitrile carbanion. The carbanionic center is practically planar; the cyano group carries a considerable negative charge, but its influence on the carbanionic center is mainly inductive. The carbanionic charge is delocalized over the phenyl ring (0.42 $e^-$), methide (0.30 $e^-$), and cyano (0.28 $e^-$) groups.

## 1. Introduction

IR data for the phenylacetonitrile carbanion were first reported in 1967 [1,2]; its cyano group frequencies were further specified for $ClMg^+$, $Li^+$, $Na^+$ and $K^+$ countercations in a variety of solvents and in the solid state [3–6]. In 1992, Croisat et al. [7] reported a detailed assignment of the IR bands in the 2300–1000 cm$^{-1}$ region of phenylacetonitrile and phenylacetonitrile-$d_5$, and of their carbanions as well. Together with $^1H$ [4] and $^{13}C$ NMR and chemical reactivity [7] data, HMO [2] and SCF MO [3,5] calculations, and Hammett-type correlations [6] the IR data for the phenylacetonitrile carbanion have been used in studies of its electronic structure (intraionic interactions) and of its ionic aggregations in solution (interionic interactions) [1–7].

In addition, ab initio force field calculations of a few nitriles [8–18] and nitrile carbanions [15] have been successfully used to study their structure [8–18] and intermolecular or interionic interactions in solution [15–18]. Ab initio MO data for either phenylacetonitrile or its carbanion have not been published up to now.

We examined (3100–2300 cm$^{-1}$) and reexamined (2300–1000 cm$^{-1}$) the IR spectra of phenylacetonitrile and of its carbanion in dimethyl sulfoxide (DMSO) and DMSO-$d_6$; the purpose of the present study is to elucidate the structure of these species on the basis of IR frequency and intensity data, and of ab initio force field calculations as well.

---

* Corresponding author.

0022-2860/95/$09.50
*SSDI* 0022-2860(94)08441-6

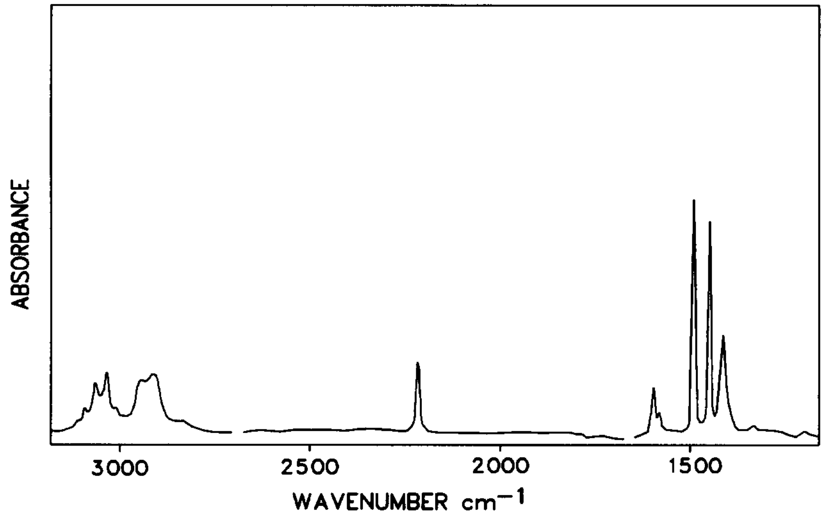


Fig. 1. IR spectrum of the phenylacetonitrile molecule.

## 2. Experimental

Commercial phenylacetonitrile, DMSO and DMSO-$d_6$ (Fluka) were distilled under reduced pressure prior to use. Dry sodium and potassium methoxides were prepared by reacting the metals with methanol and methanol-$d_4$ (Merck) and removing the excess of alcohol in vacuo. The phenylacetonitrile carbanion was prepared by adding DMSO and DMSO-$d_6$ solutions of phenylacetonitrile to an excess of dry sodium and potassium methoxides and methoxides-$d_3$. The reaction mixture was stirred and then filtered under pure argon. The equilibrium p$K_a$ difference between the methanol (29.0) and phenylacetonitrile (21.9), measured in DMSO [19], is sufficient for a practically complete metalation, which is evident on the spectrum (Figs. 1 and 2; the bands of the parent compound disappeared completely after metalation).

$$C_6H_5CH_2CN + CH_3O^-M^+$$
$$\rightleftarrows [C_6H_5CHCN]^-M^+ + CH_3OH$$
$$(M = Na \text{ and } K)$$

The presence of $CH_3OH$ ($CD_3OH$), obtained as a result of this reaction in solution, has been accounted for in the spectral treatment.

The IR spectra have been recorded using a Bruker IFS-113v Fourier transform spectrometer with $CaF_2$ cells of 0.13 mm path length.

## 3. Computations

The ab initio computations have been performed using the GAMESS software [20] at the HF 3-21G level. No scaling in the ab initio force field has been done.

As is known, for molecules with 12 or more atoms, the ab initio 3-21G data can be very valuable in vibrational assignments, structural determinations, etc.; this basis set is quite sufficient, and little is gained by using 6-31G or 6-31G* basis sets for obtaining the frequencies of the normal vibrations [21].

## 4. Results and discussion

### *4.1. Infrared spectra*

### *4.1.1. Phenylacetonitrile molecule*

The IR spectrum of phenylacetonitrile in DMSO/DMSO-$d_6$ is shown in Fig. 1. The numerical data for frequencies and intensities of the bands are listed in Table 1 together with those taken from Ref. [7]. As seen, there is good agreement between them. The neat (native, unscaled) theoretical frequency values are also listed in Table 1 for the phenylacetonitrile molecule. It is well known [8,9,12,13,15–17,21–26] that frequencies obtained by ab initio force field calculations

Table 1
Theoretical and experimental IR data for the $C_6H_5CH_2CN$ molecule

| No. | Ab initio force field | | | Experimental | | | | Ab initio force field description[e] |
|---|---|---|---|---|---|---|---|---|
| | $\nu$ (cm$^{-1}$) | $\nu^a$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | $\nu^{b,c}$ (cm$^{-1}$) | Assignment[b] | $\nu^d$ (cm$^{-1}$) | $A^d$ (km mol$^{-1}$) | |
| 1 | 3399 | 3053 | 1.8 | | | | | $\nu_{PhH}$ |
| 2 | 3373 | 3030 | 13.1 | | | 3089 | 4.0 | $\nu_{PhH}$ |
| 3 | 3362 | 3020 | 24.0 | | | 3063 | | $\nu_{PhH}$ |
| 4 | 3349 | 3008 | 4.4 | | | 3033 | | $\nu_{PhH}$ |
| 5 | 3335 | 2996 | 1.4 | | | | | $\nu_{PhH}$ |
| 6 | 3256 | 2925 | 1.0 | | | 2942 | 9.8 | $\nu^{as}_{CH_2}$ |
| 7 | 3217 | 2890 | 1.9 | | | 2907 | | $\nu^{s}_{CH_2}$ |
| 8 | 2591 | 2330 | 6.0 | 2253 m | $\nu_{CN}$ | 2248 | 4.3 | $\nu_{CN}$ |
| 9 | 1777 | 1601 | 7.9 | 1602 m | 8a | 1603 | 2.2 | $\delta_{CCC}$, $\nu_{CC}$ |
| 10 | 1755 | 1581 | 1.3 | 1586 w | 8b | 1587 | | $\delta_{CCC}$ |
| 11 | 1674 | 1509 | 25.0 | 1495 s | 19a | 1498 | 5.3 | $\nu_{CC}$, $\delta_{CCC}$, $\delta_{PhH}$ |
| 12 | 1629 | 1469 | 17.3 | 1415 s | $\delta_{CH_2}$ | 1418 | 4.5 | $\delta_{CH_2}$, $\delta_{CCC}$ |
| 13 | 1626 | 1466 | 6.8 | 1454 s | 19b | 1456 | 3.9 | $\delta_{CCC}$ |
| 14 | 1531 | 1381 | 0.9 | | | | | $\delta_{PhH}$, $\delta_{CCC}$, $\nu_{CC}$, $\delta_{CH_2}$ |
| 15 | 1462 | 1319 | 0.5 | 1336 w | 14 | 1339 | w | $\delta_{CH_2}$, $\delta_{CCC}$, $\nu_{CC}$ |
| 16 | 1424 | 1285 | 0.4 | | | | | $\delta_{CH_2}$ |
| 17 | 1356 | 1224 | 0.1 | | | | | $\delta_{CCC}$, $\nu_{CC}$ |
| 18 | 1338 | 1208 | 0.1 | 1203 w | $\nu^{a}_{PhCC}$ [f] | | | $\delta_{CCC}$, $\nu_{CC}$ |
| 19 | 1302 | 1176 | 0.1 | 1184 w | 9a | 1186 | w | $\delta_{CCC}$, $\nu_{CC}$, $\nu_{PhC}$ |
| 20 | 1239 | 1119 | 0.1 | 1157 w | 9b | 1158 | w | $\delta_{CCC}$, $\nu_{CC}$ |
| 21 | 1200 | 1084 | 1.6 | 1076 m | 18b | | | $\delta_{CCC}$ |
| 22 | 1194 | 1079 | 0.5 | | | | | $\tau_{CCCC}$, $\tau_{HCCC}$ |
| 23 | 1162 | 1050 | 0.2 | | | | | $\tau_{CCCC}$, $\tau_{HCCC}$ |
| 24 | 1143 | 1033 | 3.6 | 1029 m | 18a | | | $\nu_{CC}$, $\delta_{CCC}$ |
| 25 | 1118 | 1011 | 6.6 | 1003 w | 12 | | | $\tau_{CCCC}$, $\tau_{HCCC}$, $\delta_{CH_2}$ |
| 26 | 1106 | 1000 | 0.05 | 998 w | 5 | | | $\delta_{CCC}$, $\nu_{CC}$ |
| 27 | 1033 | 935 | 1.2 | 969 w | 17a | | | $\tau_{CCCC}$, $\tau_{HCCC}$, $\delta_{CH_2}$ |
| 28[g] | 1012 | 916 | 8.9 | 940 m | $\nu^{s}_{PhCC}$ | | | $\nu^{s}_{CCN}$ |

[a] Scaled, according to correlation Eq. (1).
[b] Ref. [7] pure liquid.
[c] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.
[d] This work, solvent DMSO and DMSO-$d_6$.
[e] Vibration modes: $\nu$, stretching; $\delta$, deformation (all kinds of); $\tau$, torsion; superscript s, symmetric; superscript as, asymmetric; the author's [7] assignment of the phenyl ring bands follows Wilson's notation.
[f] Mixed with 1 or with 12 mode.
[g] Followed by 14 lower-frequency bands.

are always higher than the experimental values. So, for a better comparison between these values, the theoretical results have usually been scaled by empirical factors [17,21,24] or by combination of empirical factors [8,9,12,13,16,21,23]. Two types of scaling have been used: (i) in the force constants [8,9,12,13,16,23]; (ii) in the resulting frequencies [17,21,22,24]. Scaling the frequencies by 0.9 gives a good result in the case of the species studied in this work. We propose, however, another type of scaling based on a linear correlation (see below, Eq. (1)). The results become statistically adjusted and, of course, better. So the scaled values in Tables 1–4 are calculated in this manner. As seen in Table 1, there is good agreement between the scaled theoretical and the experimental frequencies, reported by Croisat et al. [7] or reported in this work. The mean deviation is 23 cm$^{-1}$. The

Table 2
Theoretical and experimental IR data for the $C_6D_5CH_2CN$ molecule

| No. | Ab initio force field | | | Experimental | | Ab initio force field description[d] |
|---|---|---|---|---|---|---|
| | $\nu$ (cm$^{-1}$) | $\nu^a$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | $\nu^{b,c}$ (cm$^{-1}$) | Assignment[b] | |
| 1 | 3256 | 2925 | 1.0 | | | $\nu^{as}_{CH_2}$ |
| 2 | 3217 | 2890 | 2.1 | | | $\nu^{s}_{CH_2}$ |
| 3 | 2591 | 2330 | 5.6 | 2252 s | $\nu_{CN}$ | $\nu_{CN}$ |
| 4 | 2514 | 2261 | 1.7 | | | $\nu_{PhD}$, $\delta_{CCC}$ |
| 5 | 2500 | 2248 | 9.1 | | | $\nu_{PhD}$ |
| 6 | 2489 | 2238 | 14.0 | | | $\nu_{PhD}$ |
| 7 | 2475 | 2226 | 15.9 | | | $\nu_{PhD}$ |
| 8 | 2464 | 2216 | 0.8 | | | $\nu_{PhD}$ |
| 9 | 1728 | 1557 | 6.3 | 1577 sh | 8a | $\delta_{CCC}$, $\nu_{CC}$ |
| 10 | 1708 | 1539 | 0.04 | 1566 m | 8b | $\nu_{CC}$, $\delta_{CCC}$ |
| 11 | 1628 | 1468 | 8.7 | 1414 s | | $\delta_{CH_2}$ |
| 12 | 1510 | 1362 | 13.2 | 1380 s | 19a | $\delta_{CCC}$, $\nu_{CC}$ |
| 13 | 1506 | 1358 | 5.9 | 1347 m | 19b | $\delta_{CCC}$, $\nu_{CC}$, $\delta_{CH_2}$ |
| 14 | 1431 | 1291 | 2.4 | 1299 w | 14 | $\delta_{CCC}$ |
| 15 | 1424 | 1285 | 0.3 | | | $\delta_{CH_2}$, $\delta_{CCC}$ |
| 16 | 1278 | 1154 | 0.1 | 1162 w | 13 | $\nu_{CC}$, $\delta_{CCC}$ |
| 17 | 1228 | 1110 | 0.04 | 1130 w | mixed | $\delta_{CCC}$, $\nu_{CC}$ |
| 18 | 1185 | 1071 | 0.2 | | | $\delta_{PhD}$, $\delta_{CCC}$, $\nu_{CC}$ |
| 19 | 1081 | 978 | 2.2 | 975 w | 12 | $\tau_{CCCC}$, $\delta_{CH_2}$ |
| 20 | 1073 | 971 | 1.9 | 961 w | | $\delta_{CCC}$, $\nu_{CC}$ |
| 21 | 1009 | 914 | 6.5 | 926 m | $\nu^{a}_{PhCC}$ | $\nu^{s}_{CCN}$, $\delta_{CCC}$, $\nu_{CC}$ |
| 22 | 1008 | 913 | 0.07 | | | $\tau_{CCCC}$, $\nu^{s}_{CCN}$, $\delta_{CCC}$ |
| 23 | 983 | 890 | 0.5 | | | $\delta_{CCC}$, $\nu_{CC}$ |
| 24 | 955 | 865 | 0.5 | 872 w | 9a | $\delta_{CCC}$, $\nu_{CC}$ |
| 25 | 950 | 861 | 0.02 | | | $\tau_{CCCC}$, $\tau_{HCCC}$ |
| 26 | 935 | 847 | 3.7 | 847 m | 18b | $\delta_{CCC}$, $\nu_{CC}$ |
| 27[e] | 931 | 844 | 4.2 | 823 m | 18a | $\delta_{CCC}$ |

[a–c] See footnotes to Table 1.
[d] See footnote e to Table 1.
[e] Followed by 15 lower-frequency bands.

strongest is the $\nu_{CN}$ deviation and this result is not surprising as it is known that the $\nu_{CN}$ mode needs smaller scaling factors; 0.745 for the force constant [9] or 0.868 for the frequency [17].

The agreement with the literature assignment is also good. There is no doubt about the high-frequency ($\nu_{Ph-H}$ and $\nu_{CN}$), 8a, b and 19a, b bands. The $\delta_{CH_2}$ (scissoring) mode seems to be coupled with the $\delta_{CCC}$ ring deformation (Table 1, No. 12), but this coupling is not important: it disappears in the phenylacetonitrile-$d_5$ molecule, and nevertheless this mode is predicted at the same frequency (Table 2, No. 11) and it has really been found at the same place [7].

We did not find in the theoretical results either $\nu^{as}_{Ph-C-C}$ or $\nu^{s}_{Ph-C-C}$ modes, as indicated by the authors [7] (Table 1, Nos. 18 and 28). The $\nu_{Ph-C}$ coordinate contributes to several bands, most strongly to No. 19, but this coordinate shows no tendency to couple with the $\nu_{C-CN}$ band. However, the latter coordinate couples strongly with $\nu_{CN}$, thus the $\nu^{s}_{C-CN}$ mode seems to be localized in the band No. 28, and the corresponding $\nu^{as}_{C-CN}$ mode is indicated as $\nu_{CN}$ (No. 8). In fact there should be a band with $\nu^{s}_{Ph-C-C}$ participation, but it is predicted to be near 450 cm$^{-1}$. We do not believe, however, that such details could be predicted strictly by 3-21G neat force field calculations.

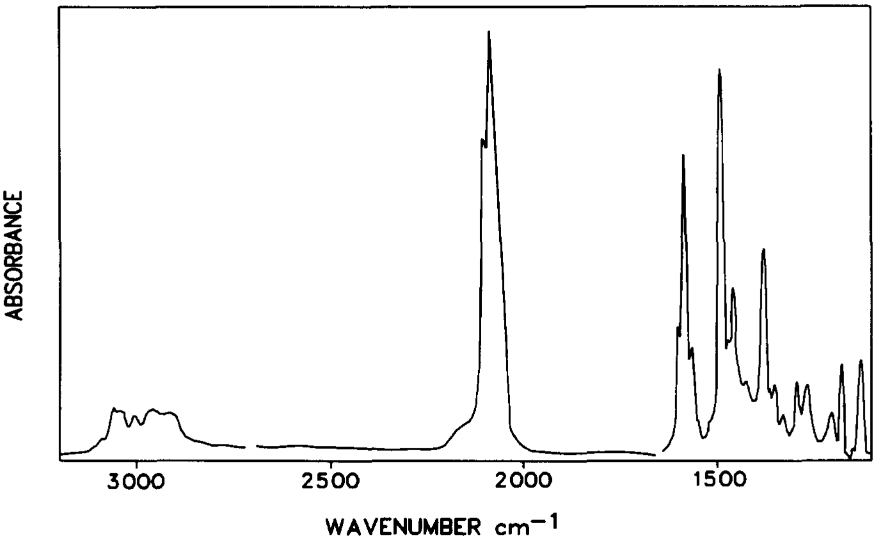


Fig. 2. IR spectrum of the phenylacetonitrile carbanion.

The found [7] and predicted frequencies of the IR bands of the phenylacetonitrile-$d_5$ molecule also agree well (Table 2). The mean deviation is $17\,\mathrm{cm}^{-1}$, while the strongest one reaches $78\,\mathrm{cm}^{-1}$ and corresponds again to the $\nu_{\mathrm{CN}}$ band. As above, the Ph–C coordinate contributes to several bands, but it does not couple strongly with the $\nu_{\mathrm{C-CN}}$ band. A band with $\nu^{\mathrm{s}}_{\mathrm{Ph-C-C}}$ participation is again predicted near $450\,\mathrm{cm}^{-1}$.

The strongest bands of the phenylacetonitrile molecule are really predicted to be strong (Table 1), but there is no quantitative agreement between the calculated and found IR band intensities (see below).

### 4.1.2. Phenylacetonitrile carbanion

The IR spectrum of the phenylaceonitrile carbanion (countercations $\mathrm{Na}^+$ or $\mathrm{K}^+$) is shown in Fig. 2. It can be seen there that conversion of phenylacetonitrile into the carbanion causes essential changes in the IR spectrum: a strong decrease in the $\nu_{\mathrm{CN}}$ frequency accompanied by a strong intensifying of the nitrile and aromatic skeletal bands. The IR spectra of sodium and potassium derivatives in DMSO (see Experimental section) are identical, so there are no strong carbanion–countercation interactions. This result confirms the assumption [7,27,28] that this carbanion either is solvent separated or a free ion in DMSO. This conclusion makes it possible to compare, in this work, the experimental IR data with the theoretical data, calculated for the free phenylacetonitrile carbanion (Tables 3 and 4).

As seen in Tables 3 and 4, there is again (as in the case of the parent molecules) a good agreement between the predicted and found IR frequencies of the phenylacetonitrile carbanion (mean deviation $20\,\mathrm{cm}^{-1}$) and for its pentadeutero analogue (mean deviation $29\,\mathrm{cm}^{-1}$). The strongest deviations are again characteristic for the $\nu_{\mathrm{CN}}$ bands, but there are some peculiarities in this case. The $\nu_{\mathrm{CN}}$ band of the non-labeled phenylacetonitrile carbanion is split into two components. The higher-frequency one seems weaker, but it is broader, so the two bands are practically equi-intense (Table 3); this splitting can be ascribed to Fermi resonance [7]. The same band in the spectrum of the deuterated carbanion appears split into three components; a strong band and two shoulders, all being assigned to $\nu_{\mathrm{CN}}$ [7]. This assignment seems bold, but it is true. The calculations predict two mixed modes, both dominated by $\nu_{\mathrm{CN}}$ (Table 4); the low-frequency one is probably Fermi split. The sum of the predicted intensities of the two bands (Nos. 6 and 7 in Table 4) is close to the intensity predicted for a single $\nu_{\mathrm{CN}}$ band (No. 7 in Table 3).

The $\nu_{\mathrm{C-H}}$ of the non-labeled carbanion contributes to band No. 2 and dominates in No. 3 (Table

Table 3
Theoretical and experimental IR data for the $C_6H_5\bar{C}HCN$ carbanion

| No. | Ab initio force field | | | Experimental | | | | Ab initio force field description[e] |
|---|---|---|---|---|---|---|---|---|
| | $\nu$ (cm$^{-1}$) | $\nu^a$ (cm$^{-1}$) | $A$ (km mol$^{-1}$ | $\nu^{b,c}$ (cm$^{-1}$) | Assignment[b] | $\nu^d$ (cm$^{-1}$) | $A^d$ (km mol$^{-1}$) | |
| 1 | 3377 | 3033 | 9.2 | | | 3056 | 4.6 | $\nu_{PhH}$ |
| 2 | 3351 | 3010 | 63.8 | | | 3041 | | $\nu_{PhH}$, $\nu_{\bar{C}H}$ |
| 3 | 3346 | 3006 | 8.8 | | | 3036 | | $\nu_{\bar{C}H}$, $\nu_{PhH}$ |
| 4 | 3337 | 2998 | 74.3 | | | 3001 | | $\nu_{PhH}$ |
| 5 | 3286 | 2952 | 54.6 | | | 2956 | 7.4 | $\nu_{PhH}$ |
| 6 | 3275 | 2942 | 31.1 | | | 2914 | | $\nu_{PhH}$ |
| 7 | 2420 | 2177 | 598.1 | 2095 m<br>2080 s | $\nu_{CN}$ | 2096<br>2078 | 79.5<br>84.3 | $\nu_{CN}$ |
| 8 | 1745 | 1572 | 346.1 | 1579 s | 8a | 1582 | 91.6 | $\delta_{CCC}$, $\nu_{CC}$ |
| 9 | 1690 | 1523 | 19.3 | 1542 w | 8b | 1566 | | $\delta_{CCC}$, $\nu_{CC}$ |
| 10 | 1649 | 1486 | 267.1 | 1484 s | 19a | 1487 | 47.3 | $\delta_{CCC}$, $\delta_{PhH}$ |
| 11 | 1621 | 1461 | 14.7 | | | 1456 | w | $\nu_{CC}$, $\delta_{PhH}$, $\delta_{CCC}$ |
| 12 | 1540 | 1389 | 137.3 | 1373 m | $\nu^a_{PhCC}$ | 1375 | 40.3 | $\delta_{PhH}$, $\nu^a_{PhCC}$, $\delta_{\bar{C}H}$, $\delta_{CCC}$ |
| 13 | 1480 | 1335 | 147.8 | 1324 w | 14 | | | $\delta_{CCC}$, $\nu_{CC}$, $\nu^a_{PhCC}$, $\delta_{PhH}$ |
| 14 | 1389 | 1254 | 68.0 | 1289 m | $\nu^s_{PhCC}$ | 1292 | w | $\nu^a_{PhCC}$, $\nu_{CC}$, $\delta_{CCC}$ |
| 15 | 1323 | 1195 | 56.3 | 1199 w | mixed | 1201 | 3.6 | $\nu_{CC}$, $\delta_{CC}$, $\delta_{PhH}$ |
| 16 | 1315 | 1187 | 94.7 | 1171 m | 9a | 1173 | 13.0 | $\delta_{CCC}$, $\nu_{CC}$ |
| 17[f] | 1281 | 1157 | 50.0 | 1147 w | 9b | | | $\delta_{CC}$, $\nu_{CC}$ |

[a–e] See foonotes to Table 1.

[f] Followed by 22 lower-frequency bands.

Table 4
Theoretical and experimental IR data for the $C_6D_5\bar{C}HCN$ carbanion

| No. | Ab initio force field | | | Experimental | | Ab initio force field description[d] |
|---|---|---|---|---|---|---|
| | $\nu$ (cm$^{-1}$) | $\nu^a$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | $\nu^{b,c}$ (cm$^{-1}$) | Assignment[b] | |
| 1 | 3348 | 3007 | 25.2 | | | $\nu_{\bar{C}H}$ |
| 2 | 2495 | 2244 | 3.8 | | | $\nu_{PhD}$ |
| 3 | 2477 | 2228 | 21.4 | | | $\nu_{PhD}$, $\delta_{CCC}$ |
| 4 | 2467 | 2219 | 32.3 | | | $\nu_{PhD}$, $\delta_{CCC}$ |
| 5 | 2429 | 2185 | 28.1 | | | $\nu_{PhD}$, $\delta_{CCC}$ |
| 6 | 2424 | 2180 | 250.3 | 2114 sh | $\nu_{CN}$ | $\nu_{CN}$, $\nu_{PhD}$ |
| 7 | 2414 | 2171 | 368.8 | 2090 s<br>2072 sh | | $\nu_{CN}$, $\nu_{PhD}$ |
| | | | | 1557 sh | 8a | |
| 8 | 1690 | 1523 | 434.7 | 1549 s | 8b | $\nu_{CC}$, $\delta_{CCC}$ |
| 9 | 1636 | 1475 | 48.3 | | | $\delta_{CCC}$, $\nu_{CC}$ |
| 10 | 1544 | 1392 | 441.8 | 1416 m | 19b | $\delta_{CCC}$, $\nu^a_{PhCC}$ |
| 11 | 1493 | 1347 | 193.6 | 1351 w | mixed | $\nu_{CC}$, $\delta_{CCC}$ |
| 12 | 1445 | 1304 | 15.1 | 1267 w | | $\delta_{CCC}$, $\nu_{CC}$ |
| 13 | 1337 | 1207 | 129.4 | 1258 m | $\nu^s_{PhCC}$ | $\delta_{CCC}$, $\nu^a_{PhCC}$ |
| 14[e] | 1272 | 1149 | 45.8 | 1170 m | 9a | $\delta_{CCC}$, $\nu_{CC}$ |

[a–c] See footnotes to Table 1.

[d] See foonote e to Table 1.

[e] Followed by 25 lower-frequency bands.

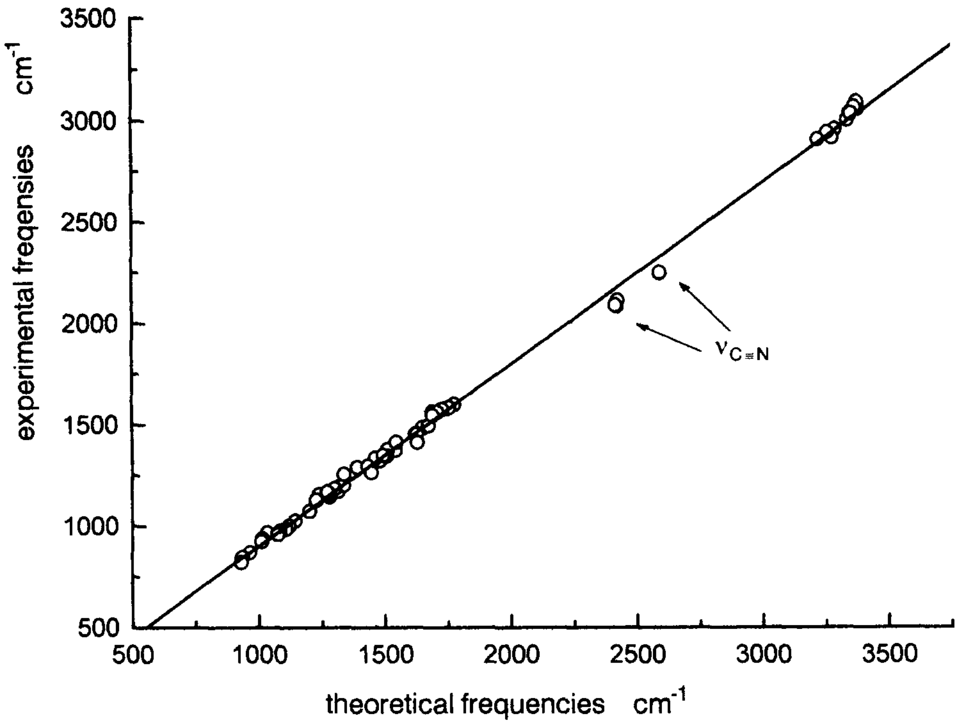


Fig. 3. Plot of experimental vs. theoretical IR frequencies of the species studied.

3). Of course, this vibration is fully localized in the deuterated carbanion (Table 4, No. 1), its band is predicted at the place of No. 3 (Table 3). The $\delta_{C-H}$ coordinate is delocalized over several modes (Nos. 11–14 (Table 3) and 10–15 (Table 4)); most of its contributions are weak and are not indicated in Tables 3 and 4.

As a result of the increase in the Ph–C and C–CN bond indices (see below), the method used predicts a contribution (although weak) of $\nu^{as}_{Ph-C-C}$ to several bands above 1200 cm$^{-1}$: Nos. 12–14 (Table 3) and 10 and 13 (Table 4). $\nu^{s}_{Ph-C-C}$ of the carbanion (like $\nu^{s}_{Ph-C-C}$ of the neutral molecule) contributes to low-frequency bands only (near 500 cm$^{-1}$ and lower). $\nu^{s}_{C-CN}$ contributes to bands predicted in the 1015–1070 cm$^{-1}$ region.

Comparing calculated and measured IR intensities of phenylacetonitrile and of its carbanion (Table 1 and 3) shows that the method used predicts well the strong increase in intensity of the $\nu_{CN}$ bands 8a, b and 19a, b, which accompanies the conversion of the phenylacetonitrile molecule to the carbanion (predicted: 100, 40 and 80 fold; found: 38, 42 and 5 fold, respectively). The method, however, fails in the prediction of the changes in the $\nu_{Ph-H}$ and $\nu_{C-H}$ band intensities (predicted: 5 and 3 times increase; found: a slight decrease). Nevertheless, we have found a linear correlation between predicted and found intensity values for the whole series of bands (see below).

### *4.1.3. Correlation analysis*

Comparing calculated and measured IR frequencies for the four species studied (two molecules and two carbanions) shows that they correlate linearly (Fig. 3). According to Jaffe's classification [29], the correlation is excellent:

$$[\nu(\text{experimental})]\,\text{cm}^{-1} = [0.8952\,(\text{ab initio}) + 10.2]\,\text{cm}^{-1} \qquad (1)$$

with values of $R = 0.9989$ (correlation coefficient); s.d. $= 32.9$ cm$^{-1}$ (standard deviation); $n = 61$ (number of data points). The strongest deviations are typical for the $\nu_{CN}$ bands (Fig. 3); these deviations have been discussed above. As mentioned, we have used

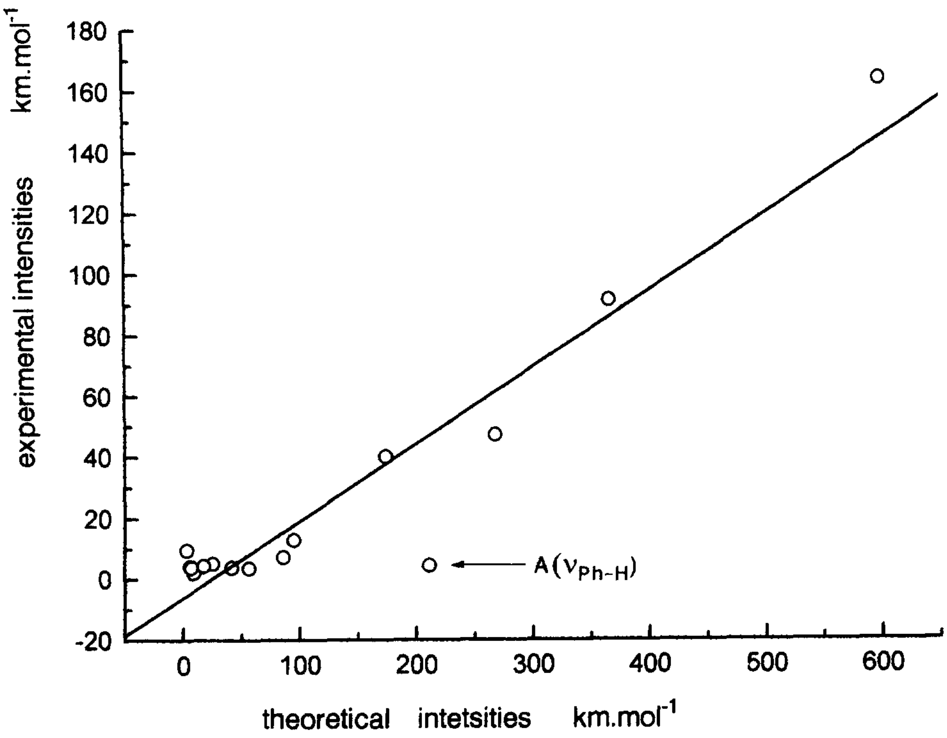


Fig. 4. Plot of experimental vs. theoretical integrated IR intensities of the species studied.

this correlation to scale the neat theoretical frequency values (Tables 1–4).

The correlation between the calculated and found IR intensities is fair (Fig. 4):

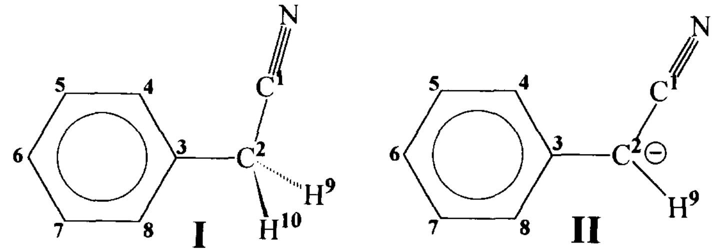
$$[A(\text{experimental})]\ \text{km mol}^{-1}$$

$$= [0.2520A(\text{ab initio}) - 5.9]\ \text{km mol}^{-1} \qquad (2)$$

with $R = 0.9464$; s.d. $= 14.3\ \text{km mol}^{-1}$; $n = 15$. The strongest is the deviation of the point, corresponding to the intensity of the $\nu_{\text{Ph-H}}$ (and $\nu_{\text{C-H}}$) bands (Fig. 4). It has been reported [8] that ab initio calculations cannot give an adequate description of the $\nu_{\text{carbon-hydrogen}}$ band intensities.

### *4.2. Structure of the phenylacetonitrile molecule and of its carbanion*

As the ab initio 3-21G method used describes well the force field of the phenylacetonitrile molecule and of its carbanion we believe that the description of the structures of these species, given by the same method, should also be adequate (Scheme 1).



Scheme 1. Ab initio steric structure of the phenylacetonitrile molecule and of its carbanion.

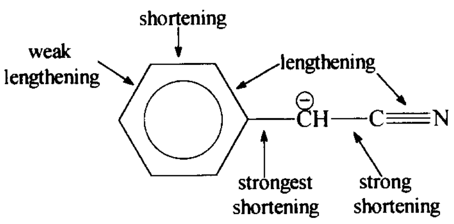
Table 5
Ab initio 3-21G steric structure parameters of the phenylacetonitrile molecule (I) and of its carbanion (II)

| Internuclear distances (Å) and dihedral angles (deg) | Molecule | Carbanion | Angles (deg) | Molecule | Carbanion |
|---|---|---|---|---|---|
| $r(C^1N)$ | 1.139 | 1.156 | $< NC^1C^2$ | 179.6 | 179.5 |
| $r(C^1C^2)$ | 1.458 | 1.389 | $< C^1C^2C^3$ | 114.1 | 123.8 |
| $r(C^2C^3)$ | 1.528 | 1.412 | $< C^2C^3C^4$ | 122.8 | 123.6 |
| $r(C^3C^4)$ | 1.382 | 1.422 | $< C^2C^3C^8$ | 117.8 | 121.2 |
| $r(C^3C^8)$ | 1.389 | 1.421 | $< C^3C^4C^5$ | 120.2 | 121.8 |
| $r(C^4C^5)$ | 1.386 | 1.375 | $< C^3C^8C^7$ | 120.5 | 122.0 |
| $r(C^5C^6)$ | 1.381 | 1.389 | $< C^4C^5C^6$ | 120.4 | 121.8 |
| $r(C^6C^7)$ | 1.386 | 1.389 | $< C^5C^6C^7$ | 119.6 | 117.6 |
| $r(C^7C^8)$ | 1.381 | 1.375 | $< C^6C^7C^8$ | 120.0 | 121.6 |
| $r(C^2H^9)$ | 1.085 | 1.073 | $< C^4C^3C^8$ | 119.3 | 115.0 |
| $r(C^2H^{10})$ | 1.085 | – | $< H^9C^2C^3$ | 109.2 | 117.1 |
| $< H^9(C^2C^1C^3)$ | 53.9 | 2.0 | $< H^{10}C^2C^3$ | 109.2 | – |
| $< H^{10}(C^2C^1C^3)$ | –53.9 | – | $< H^9C^2H^{10}$ | 107.8 | – |

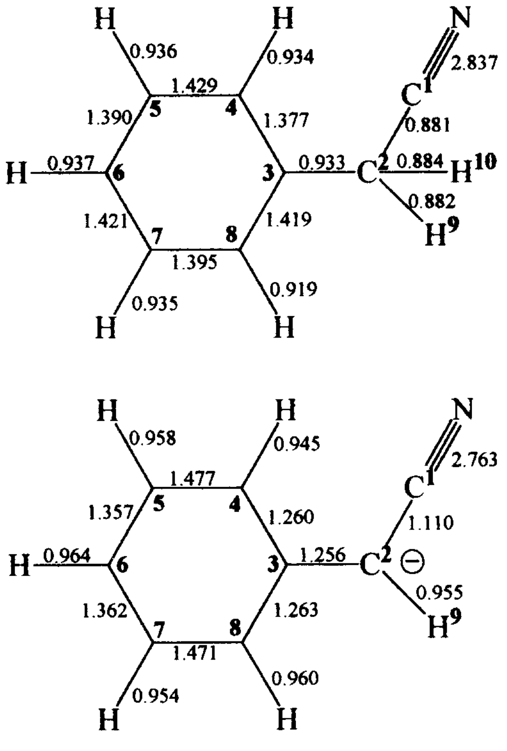
For atom numbering see Scheme 1.

The geometrical structure parameters of the species studied are listed in Table 5. It can be seen there that the conversion of the phenylacetonitrile molecule into the carbanion leads to a change in the configuration of the $C^2$ atom: from tetrahedral in the molecule it becomes planar in the carbanion, as in the case of tricyanomethane and its carbanion [30] (cf. the dihedral and other angles at $C^2$; for example: the $C^2-H^9$ bond in the carbanion is predicted to deviate from the $C^2C^1C^3$ plane by 2° only).

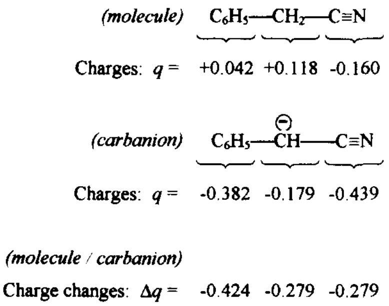
The bond length changes, which accompany the conversion of phenylacetonitrile into carbanion, are illustrated in Scheme 2. The benzene ring bond length changes are qualitatively similar to those reported by Krygowski et al. [31] for the nitrophenolate anion on the basis of X-ray diffraction.



Scheme 2. Bond length changes accompanying the conversion of the phenylacetonitrile molecule into carbanion.



Scheme 3. Ab initio bond indices of the phenylacetonitrile molecule and of its carbanion.



$$\textit{(molecule)}\quad \underbrace{C_6H_5}-\underbrace{CH_2}-\underbrace{C\equiv N}$$

Charges: $q =$ +0.042 +0.118 -0.160

$$\textit{(carbanion)}\quad \underbrace{C_6H_5}-\underbrace{\overset{\ominus}{C}H}-\underbrace{C\equiv N}$$

Charges: $q =$ -0.382 -0.179 -0.439

*(molecule / carbanion)*

Charge changes: $\Delta q =$ -0.424 -0.279 -0.279

Scheme 4. Ab initio net charges of the phenylacetonitrile molecule and of its carbanion.

The molecule → carbanion bond index variations are in agreement with the corresponding bond length changes. The largest increases are in the $C^2-C^3$ and $C^1-C^2$ bond indices and they correspond to the strongest shortening of the same bonds (cf. Schemes 2 and 3).

Comparing the total $(\sigma + \pi)$ net charge distribution over the phenylacetonitrile molecule and over its carbanion gives an interesting result. As seen from Scheme 4, the cyano group carries the largest negative charge in the carbanion, but it has already had a considerable charge in the neutral molecule, due to its strong inductive effect. The calculations of the distribution of the total net charge changes, which accompany the conversion of the neutral phenylacetonitrile molecule to its carbanion, give another result: the great part of the carbanionic charge, $0.424\,e^-$; is delocalized over the benzene ring, whereas the methide and the cyano groups hold smaller parts of it, $0.297\,e^-$ and $0.279\,e^-$ respectively. This conclusion is in agreement with the above discussed results: the strongest changes in both the bond length and bond index take place at the $C^2-C^3$ bond. Qualitatively similar results have been reported by Abbotto et al. [28] on the basis of NMR data for the phenylaceonitrile carbanion.

## 5. Conclusion

The ab initio force field calculations give a good description of the IR spectra and, we believe, of the structure of phenylacetonitrile and of its carbanion. Such calculations, at the 3-21G level, will be very useful in the case of other reaction intermediates (ions and radicals), for which force fields are not determined, and for which experimental (X-ray diffraction etc.) steric structure parameters are inaccessible or unknown. The excellent correlation found could be used for estimation of the vibrational frequencies of related molecules and ions.

## References

[1] C. Krueger, J. Organomet. Chem., 9 (1967) 125.

[2] I.N. Juchnovski, Teor. Eksp. Khim., 3 (1967) 410.

[3] I.N. Juchnovski and I.G. Binev, C.R. Acad. Bulgare Sci., 26 (1973) 659.

[4] G. Albagnac, B. Brun, B. Calas and L. Giral, Bull. Soc. Chim. Fr., (1974) 1469.

[5] I.N. Juchnovski and I.G. Binev, J. Organomet. Chem., 99 (1975) 1.

[6] I.N. Juchnovski, I.G. Binev and Ts.M. Kolev, Tetrahedron Lett., (1976) 1519.

[7] D. Croisat, J. Seyden-Penne, T. Strzalko, L. Wartski, J. Corset and F. Froment, J. Org. Chem., 57 (1992) 6435.

[8] B.A. Hess, Jr., L.J. Schaad, P. Carsky and R. Zahradnik, Chem. Rev., 86 (1986) 709.

[9] J.R. Durg, W. Zhao and T.S. Little, Chem. Phys., 128 (1988) 335.

[10] M.N. Ramos, B.B. Neto, A.M. Simas and R.E. Bruns, J. Mol. Struct., 175 (1988) 355.

[11] P. Raeymaekers, H. Figeys and P. Geerlings, J. Mol. Struct. (Theochem), 169 (1988) 509.

[12] T.S. Little, W. Zhao and J.R. Durig, J. Raman Spectrosc., 19 (1988) 479.

[13] A.G. Csaszar and G. Fogarasi, Spectrochim. Acta, Part A, 45 (1989) 845.

[14] O.M. Herrera, R.E. Bruns and B.B. Neto, J. Chem. Phys., 90 (1989) 6933.

[15] G. Raabe, E. Zobel, J. Fleischhauer, P. Gerdes, D. Mannes, E. Mueller and D. Enders, Z. Naturforsch., Teil A, 46 (1990) 275.

[16] M.A. Ablaeva, A.G. Pelminshchikov, G.M. Zhidomirov, E.B. Burgina and V.P. Baltakhiniov, React. Kinet. Catal. Lett., 47 (1993) 99.

[17] D. Mathieu, M. Defranceschi, G. Lecayon and J. Delhalle, C.R. Acad. Sci. Paris, Ser. 2, 315 (1992) 1181.

[18] M. Defranceschi, D. Peeters, D. Mathieu, J. Delhalle and G. Lecayon, J. Mol. Struct. (Theochem), 287 (1993) 153.

[19] F.G. Bordwell, Acc. Chem. Res., 21 (1988) 456.

[20] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koeski, N. Matsunaga, K.A. Nguyen, S. Su, L.T. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem., 14 (1993) 1347.

[21] J.R. Durig, M.J. Lee, H.M. Badawi, J.F. Sullivan and D.T. Durig, J. Mol. Struct., 266 (1992) 59.

[22] D.J. DeFrees and A.D. McLean, J. Chem. Phys., 82 (1985) 333.

[23] P. Csaszar, A. Csaszar and L. Harasanyi, J. Mol. Struct. (Theochem), 136 (1986) 323.

[24] E. Cebe, Tr. J. Phys., 16 (1992) 327.

[25] S.P. Gejji, K. Hermansson and J. Lindgren, J. Phys. Chem., 97 (1993) 3712; 6986.

[26] L. Turi and J.J. Dannenberg, J. Phys. Chem., 97 (1993) 12197.

[27] I.G. Binev, Ph.D. Thesis, Bulgarian Academy of Sciences, Sofia, 1974, p. 108.

[28] A. Abbotto, S. Bradamante and G. Pagani, J. Org. Chem., 58 (1993) 449.

[29] H.H. Jaffe, Chem. Rev., 53 (1953) 191.

[30] J. Cioslwski, S.T. Mixon and E.D. Fleischmann, J. Am. Chem. Soc., 113 (1991) 4751.

[31] T.M. Krygowski and I. Turowska-Tyrk, Collect. Czech. Chem. Commun., 55 (1990) 165; T.M. Krygowski, M.K. Kalinowski, I. Turowska-Tyrk, C. Hiberty, P. Milart, A. Silvestro, R.D. Topsom and S. Daehne, Struct. Chem., 2 (1991) 71.