Journal of Molecular Structure, 18 (1973) 429–434

ON THE STRUCTURE OF PHENYLISOCYANIDE

B. BAK, B. P. VAN EIJCK* AND C. KIERKEGAARD

Chemical Laboratory V, University of Copenhagen, The H. C. Ørsted Institute, DK-2100, Copenhagen (Denmark)

(Received 7 May 1973)

ABSTRACT

Microwave spectra of phenylisocyanide, $C_6H_5\overset{+}{N}\equiv\overset{-}{C}$ (I), 2-D-phenylisocyanide, 2,4-D_2-phenylisocyanide, and 2,4,6-D_3-phenylisocyanide were recorded and analyzed. Assuming the structural identity of the $C_6H(3)H(4)H(5)$ fragments of I and of phenylcyanide (II). A C(1)–N distance of 1.410 Å and an $\overset{+}{N}\equiv\overset{-}{C}$ distance of 1.142 Å followed. The effects of changing some of the assumptions are discussed.

INTRODUCTION

A complete determination of the structure of phenylisocyanide, $C_6H_5\overset{+}{N}\equiv C$ (I), by a spectroscopic method would involve an investigation of nine sufficiently enriched isotopic species as in the case of phenylcyanide (II)[1, 2]. In this paper the results of recording and analyzing microwave spectra of phenylisocyanide (I) and of a mixture of 2-D-phenylisocyanide, 2,4-D_2-phenylisocyanide, and 2,4,6-D_3-phenylisocyanide are reported. Based on the rotational constants derived and on the assumption that the geometry of the $C_6H(3)H(4)H(5)$ fragment of II is conserved in I, C(1)–N and $\overset{+}{N}\equiv\overset{-}{C}$ distances were calculated.

The choice of inertial system and the numbering of atoms is strictly analogous to those used in ref. 1, substitution occurring at C(1).

EXPERIMENTAL

Compound I was prepared according to Appel et al.[3]. The mixture of deuterated isocyanides was prepared from 2-amino-benzoic acid. 15 g of the acid was boiled for 5 h with 21.6 g D_2O under reflux. The water was removed in vacuo

---

* On leave of absence from the Laboratorium voor Kristalchemie, University of Utrecht, The Netherlands.

TABLE 1

FORMULAE, NOTATION AND PERCENTAGE OF PHENYLISOCYANIDE AND THREE DEUTERATED SPECIES

Number and type of transitions studied and maximum rotational quantum number $J_{\max}$ involved. Spectral region: 12–40 GHz[a].

Compound	*Species*		*Number of observed transitions*		$J_{\max}$
	Notation	*Percentage*	*R-type*	*Q-type*	
phenylisocyanide	I	100	30	19	39
[2-D]-phenylisocyanide	III	~20	21	7	34
[2,4-D_2]-phenylisocyanide	IV	~40	14	0[b]	10
[2,4,6-D_3]-phenylisocyanide	V	~40	18	0[b]	10

[a] Each transition is assigned with an accuracy of 2–3 ppm. Measured frequencies are available from the authors on request.
[b] See text.

and the H–D exchange procedure repeated. The resulting deuterated 2-aminobenzoic acid yielded, upon decarboxylation[4] at 180 °C (4 h), 7.0 g vacuum-distilled product (69 % yield). After routine formylation of the product it was converted to a ca. 1 : 2 : 2 mixture of 2-D-, 2,4-D_2-, and 2,4,6-D_3-phenylisocyanide, purified by distillation in vacuo (yield 2.4 g (33 %)). Its isotopic composition followed roughly from the microwave spectrum. Lines from parent I were not observed.

TABLE 2

STANDARD DEVIATION (rms), ROTATIONAL CONSTANTS (MHz), CENTRIFUGAL DISTORTION CONSTANTS (kHz), PRINCIPAL MOMENTS OF INERTIA, INERTIAL DEFECT (μÅ^2)[a] AND ASYMMETRY PARAMETER κ FOR PHENYLISOCYANIDE AND THREE ISOTOPIC SPECIES (Table 1)

	Phenylisocyanide	*III*	*IV*	*V*
rms	0.056	0.062	0.047	0.095
A	5659.5190±0.0056	5384.321 ±0.014	5384.564 ±0.030	5129.733 ±0.054
B	1639.7757±0.0012	1638.7005±0.0023	1583.367 ±0.002	1582.291 ±0.003
C	1271.1538±0.0012	1256.1018±0.0022	1223.344 ±0.001	1209.064 ±0.002
T_4	0.8526±0.0090	0.775 ±0.017	0[b]	0[b]
T_5	−0.0473±0.0038	−0.027 ±0.011	0[b]	0[b]
I_a	89.29664±0.00009	93.86067±0.00025	93.8564±0.0005	98.519 ±0.001
I_b	308.19826±0.00023	308.40046±0.00043	319.1781±0.0004	319.3950±0.0006
I_c	397.57266±0.00039	402.33683±0.00072	413.1102±0.0003	417.9896±0.0006
I.D.	0.07770±0.00022	0.07570±0.00055	0.0756[b]	0.0756[b]
κ	−0.8320004±0.0000002	−0.8146422±0.0000004	−0.826963±0.000002	−0.809610±0.000005

[a] Conversion factor: 505376 μÅ^2 MHz.
[b] Assumed value[2].

The microwave spectrograph was of the conventional Stark-modulated (50 kHz) type. The region 12–40 GHz was scanned. Pressures from 3–20 μ were applied, the spectrum of I was recorded at -7 °C and the remaining spectra at room temperature. Species formulae, notation and percentages are reported in Table 1 which, in addition, gives the number and type of observed transitions and $J_{\max}$, the highest rotational quantum number in the analysis. Corrections for centrifugal distortion were calculated using a least-squares analysis[5]. For species I and III sufficiently accurate reproduction of experimental data was obtained for $T_1 = T_2 = T_3 = 0$ (T_i's defined in ref. 2) while T_4 and T_5 differed from zero (Table 2). For the rather incomplete spectra of the species IV and V for which Q-lines were observed but not measured, centrifugal distortion was small enough to be ignored. To achieve a reliable value of the rotational constant, A, of these species the inertial defect was chosen in agreement with III (Table 2).

MOLECULAR STRUCTURE

Due to the intimate resemblance of the vibrational spectra of I and II documented elsewhere[6] considerable, but quantitatively unknown, structural similarity of I and II is to be expected. This is further substantiated by the experimental microwave results. Table 3 reports the coordinates of H(2), H(4), and H(6) in the inertial system of I which may be derived from the data of Table 2.

TABLE 3

H(2), H(4) AND H(6) SUBSTITUTION COORDINATES (in Å) IN PHENYLISOCYANIDE (I) AND PHENYLCYANIDE (II) INERTIAL SYSTEMS

Numbering of atoms as in ref. 1. Calculated H(2)–H(4) and H(2)–H(6) distances (Å).

	I			*II*		
	H(2)	*H*(4)	*H*(6)	*H*(2)	*H*(4)	*H*(6)
a	-0.4457^{a}	3.2841^{b}	-0.4444^{c}	-0.3995	3.3186	-0.3995
b	2.1410	0	-2.1412	2.1455	0	-2.1455
Distances						
H(2)–H(4)		4.3000			4.2927	
H(2)–H(6)		4.2820			4.2910	

[a] Data from species I and III. Replaced by -0.4450 in the above calculations and in Table 4.
[b] Data from species I, III and IV.
[c] Data from species I, III, IV and V. Replaced by -0.4450 in calculations.

The coordinates of the corresponding hydrogen atoms in II (in the inertial system of II) are also quoted. For both molecules the H(2)–H(4) and the H(2)–H(6) distances were calculated, and found to be equal within $2\,^0/_{00}$. Also, $I_a = 89.36076$ and 89.29664 μÅ^2 for II and I, respectively, differ by only 0.06412 μÅ^2. Here, the slightly different b-values of H(2) and H(6) account for $2m_H(2.1455^2 - 2.1411^2) = 0.0377$ μÅ^2 of this difference leaving 0.0264 μÅ^2 unexplained. In terms of a displacement of, say, C(2) and C(6) by β Å from their positions in II toward the a-axis this means $\beta = 0.0004$ Å or close to the error of this coordinate[2]. Of course, contributions to $I_a(\mathrm{II}) - I_a(\mathrm{I})$ from much larger displacements of off-axis atoms may accidentally cancel or almost so.

Using our initial assumption of equal $C_6H(3)H(4)H(5)$ fragments of I and II and noting that the b-coordinate of H(4) in the inertial system of II is 3.3186 Å while the b-coordinate of H(4) in the inertial system of I is $\delta = 0.0345$ Å *less*, we have summarized the assumed coordinates in the latter inertial system with the ones obtained experimentally in the present investigation in Table 4.

TABLE 4

ADOPTED ATOMIC COORDINATES a, b (in Å) IN THE INERTIAL SYSTEM OF PHENYLISOCYANIDE

Numbering of atoms as in ref. 1.

	$C(1)$	$C(2)$	$C(3)$	$C(4)$	$H(2)$	$H(3)$	$H(4)$
a	−0.5640[a]	0.1106[a]	1.5062[a]	2.2045[a]	−0.4450[c]	2.0489[a]	3.2841[c]
b	0	1.2126[b]	1.2105[b]	0	2.1411[c]	2.1467[b]	0

[a] From phenylcyanide[2] by subtracting 0.0345 Å (= δ).
[b] From phenylcyanide[2].
[c] From this investigation.

If the coordinates of H(2) were also carried over from the inertial system of II to I as done for H(3) we would get $a = -0.4340$ and $b = 2.1455$ Å, the deviation of the a-coordinate being 0.011 Å, and the deviation of the b-coordinate being 0.004 Å from our experimental values. These deviations may be real and consistent with our initial assumption, but they may also indicate that fragment identity is not strictly fulfilled.

The required a-coordinates of N and C(7) must obey two conditions. In the first place, the centre of mass is at (0, 0, 0). Secondly, since the coordinates of Table 4 are derived from "substitution" coordinates the experimental value of $I_b = 308.19826$ μÅ^2, corrected as in ref. 2 by 0.17 per cent to 307.67432 μÅ^2, must be reproduced. The results obtained are reported in Table 5.

TABLE 5

$C(1)\text{–}\overset{+}{N}$ and $\overset{+}{N}\equiv\overset{-}{C}(7)$ distances (in Å) in phenylisocyanide as calculated (1) under assumptions mentioned in this paper; (2) changing $\delta = 0.0345$ (see text) to 0.0350; (3) changing the a-coordinate of C(1) by +0.002 Å; (4) correcting I_b's experimental value by 0.32 per cent instead of 0.17 per cent

		Distances	
		$C(1)\text{–}\overset{+}{N}$	$\overset{+}{N}\equiv\overset{-}{C}(7)$
Condition	(1)	1.410	1.142
Condition	(2)	1.400	1.160
Condition	(3)	1.416	1.136
Condition	(4)	1.407	1.149

DISCUSSION

Not many "pairs" of cyanide–isocyanides have hitherto been investigated. For CH_3CN and $CH_3\overset{+}{N}\equiv\overset{-}{C}$, a C≡N distance of 1.158 Å and an $\overset{+}{N}\equiv\overset{-}{C}$ distance of 1.167 Å respectively were found[7]. Using assumptions previously specified[8] microwave spectra of *tert.*-C_4H_9CN and of *tert.*-$C_4H_9\overset{+}{N}\equiv\overset{-}{C}$ are interpretable in terms of a C≡N distance of 1.149 Å and an $\overset{+}{N}\equiv\overset{-}{C}$ distance of 1.166 Å, respectively. In both cases $C\equiv N < \overset{+}{N}\equiv\overset{-}{C}$. In phenylcyanide[2] the C≡N distance is 1.158 Å. Since the $\overset{+}{N}\equiv\overset{-}{C}$ distance of phenylisocyanide may be at least equally long, model (2) of Table 5 makes the better sense. The corresponding C(1)–N distance of 1.400 Å agrees with an estimate based on covalent radii[9]. According to this philosophy the predicted C(1)–N distance is $1.451-0.055 = 1.396$ Å where 1.451 Å is the observed C(1)–C(7) distance in phenylcyanide[2] while 0.055 Å is an average difference between carbon and nitrogen "covalent radii".

ACKNOWLEDGEMENT

We are indebted to Dr. F. Mata the University of Valladolid, Spain, for his participation in this work in its early stages.

REFERENCES

1 B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Chem. Phys.*, 37 (1962) 2027.
2 J. Casado, L. Nygaard and G. O. Sørensen, *J. Mol. Structure*, 8 (1971) 211.
3 R. Appel, R. Kleinstück and K. D. Ziehn, *Angew. Chem.*, 83 (1971) 143.
4 A. Sultanov, *J. Gen. Chem. (U.S.S.R.)*, 16 (1946) 1835.

5 G. O. Sørensen, *ROTFIT centrifugal distortion program*, 1972, available on request.
6 B. Bak and C. Kierkegaard, *Acta Chem. Scand.*, in press.
7 W. Kessley, H. Ring, R. Trambarulo and W. Gordy, *Phys. Rev.*, 79 (1950) 54.
8 B. Bak, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, 2 (1958) 54.
9 B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.*, 33 (1960) 418.

NOTE ADDED IN PROOF

Using a large basis set (11s 6p 1d/6s 3p 1d) and including configuration interaction, P. K. Pearson, G. L. Blackman, H. F. Schaefer and U. Wahlgren have optimized the geometries of HCN and HNC, finding a H–C and a C≡N distance of 1.068 and 1.153 Å for HCN, while the H–$\overset{+}{\mathrm{N}}$ and $\overset{+}{\mathrm{N}}\equiv\overset{-}{\mathrm{C}}$ distances of HNC were calculated as 0.995 and 1.169 Å.