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p-(Tricyanovinylidene)phenylhydrazones. Nucleophilic Attack on Carbon—Carbon Double Bonds**

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The dispacement of a —CN group in *p*-(tricyanovinylidene)-phenylhydrazones, induced by amines, is investigated. The rate of the reaction is dependent on the polarity of the solvent and the observed second-order rate coefficients k^2_{obs} for the —CN displacement increase with the amine concentration. A X-ray analysis of one of the substituted compounds is also reported.

(Keywords: Hydrazones; Nucleophilic substitution reactions; Kinetics of substitution reactions)

p-(Tricyanovinyliden)phenylhydrazone. Nukleophiler Angriff auf die C—C*-Doppelbindung*

Es wird die Substitution einer —CH-Gruppe in *p*-(Tricyanovinyliden)phenylhydrazonen mit Aminen geprüft. Die Reaktionsgeschwindigkeit wird von der Polarität des Lösungsmittels bestimmt; die berechneten Geschwindigkeitskoeffizienten zweiter Ordnung $k^2_{\text{ber.}}$ (Substitution der —CN-Gruppe) nehmen mit der Aminkonzentration zu. Es wird die Röntgenstrukturanalyse eines Adduktes beschrieben.

Introduction

Cyanovinyl derivatives of aromatic amines are compounds of interest in the formation of Charge-Transfer complexes (CTC) [1], for their dyeing properties [2] and conductivity at low temperatures [3]. Nucleophilic vinylic displacement (via addition-elimination route) of a cyano group by

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amines, in tricyanovinylarylamines, has been investigated and a mechanism proposed on the basis of kinetic determinations (the formation of an intermediate zwitterion has been hypothesized) [4].

In a previous paper [5] we described the synthesis and characterization of tricyanovinyl derivatives of phenylhydrazones; these deeply coloured compounds have good dyeing properties (unpublished results) while do not show a π-amphoteric character in the formation of CTC [6] (as the cited tricyanovinylarylamines do [7]) probably due either to the low charge density on the hydrazono group and to the extended charge delocalization (electrochemical and charge distribution studies are in progress).

In this work we report a study of —CN group nucleophilic displacement in *p*-(tricyanovinylidene)phenylhydrazones induced by aromatic and aliphatic amines together with a X-ray analysis of one derivative.

Results and Discussion

Four representative tricyanovinyl derivatives of benzaldehyde and benzophenone phenyl- and methylphenylhydrazones (**I**–**IV**) were left to react with the amines listed in Table 1. In all cases the end of the reaction was evidenced by the change of the colour from deeply red to light yellow. Table 1 reports the most characteristic properties of the reaction products; the IR absorptions of the starting tricyanovinyl compounds are also listed.

In analogy to literature reports [4], with a sluggish leaving group like —CN, the mechanism shown in Scheme 1 may be presumed.

Scheme 1

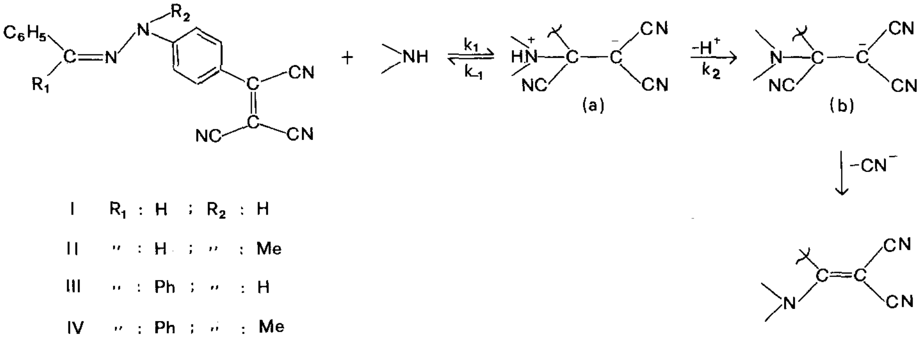

Table 1. *Data of the reaction products and IR of the starting tricyanovinyl compounds*

Tricyanovynil Compound	Amines	MP (°C)	Solvent	Elemental Analysis Calc/Found %			Formula	IR absorption bands, cm^{-1}			
				C	H	N		NH	CN	C=C	C=N
I								3320	2200		1590
1	Diethylamine	130-2	EtOH	73.43 73.21	6.16 6.20	20.34 20.08	$C_{21}H_{21}N_5$	3275	2222 2218	1615	1598 1578w
2	Pyrrolidine	190	EtOH	73.87 73.32	5.61 5.55	20.52 20.73	$C_{21}H_{19}N_5$	3303	2200 2188	1612	1600 1585
3	Piperidine	215	EtOH	74.34 73.69	5.95 6.10	19.71 19.72	$C_{22}H_{21}N_5$	3260	2205 2193	1610	1595 1587
4	Morpholine	208-10	EtOH	70.57 69.92	5.36 5.31	19.60 19.40	$C_{21}H_{19}N_5O$	3270	2203 2190	1609	1594 1577w
5	p-Anisidine	212	EtOH	73.26	4.87	17.80	$C_{24}H_{19}N_5O$	3280/60	2215 2197	1613	1596
II									2205		1587
6	Diethylamine	187-90	EtOH	73.92 73.32	6.48 6.57	19.60 19.52	$C_{22}H_{23}N_5$		2220/2212	1610	1602 1593
7	Pyrrolidine	240-50	EtOH	74.34 73.94	5.96 6.10	19.71 19.32	$C_{22}H_{21}N_5$		2203/2185	1612	1598 1585w
8	Piperidine	203-5	EtOH	74.77 74.94	6.27 6.38	18.96 19.07	$C_{23}H_{23}N_5$		2198 2185	1603	1580
9	Morpholine	198-9	C_6H_6	71.13 71.88	5.70 5.87	18.85 18.67	$C_{22}H_{21}N_5O$		2195 2182	1602	1570
10	p-Anisidine	250-3	EtOH	73.69 73.67	5.19 5.35	17.19 17.07	$C_{25}H_{21}N_5O$		2215 2195	1615	1585
III								3270	2208		1560
11	Diethylamine	129-31	EtOH	77.29 76.97	6.01 6.13	16.70 16.77	$C_{27}H_{25}N_5$	3391	2212 2197	1612	1572w
12	Pyrrolidine	180-3	EtOH	77.67 77.20	5.55 5.44	16.78 16.76	$C_{27}H_{23}N_5$	3340	2209 2191	1613	1583w
13	Piperidine	227-9	EtOH	77.93 77.49	5.84 5.78	16.23 16.44	$C_{28}H_{25}N_5$	3260	2212 2197	1609	1580w
14	Morpholine	238-40	C_6H_6	74.80 75.02	5.35 5.31	16.16 16.04	$C_{27}H_{23}N_5O$	3270	2215 2200	1610	1604 1580w
15	p-Anisidine	188-90	EtOH	76.74 76.09	4.94 4.97	14.92 14.59	$C_{30}H_{23}N_5O$	3280/60	2222 2190	1612	1595
IV									2219		1575
16	Diethylamine	151-2	EtOH	77.56 77.31	6.28 6.40	16.16 16.23	$C_{28}H_{27}N_5$		2204 2190	1607	1595
17	Pyrrolidine	213-15	EtOH	72.92 77.51	5.83 6.03	16.23 16.35	$C_{28}H_{25}N_5$		2200 2183	1608	1595
18	Piperidine	229-30	EtOH	78.17 77.68	6.11 6.15	15.72 15.52	$C_{29}C_{27}N_5$		2203 2188	1608	1596
19	Morpholine	235-8	EtOH	75.14 74.91	5.63 5.76	15.65 15.80	$C_{28}H_{25}N_5O$		2208 2200	1603	
20	p-Anisidine	210	EtOH	76.99 76.47	5.21 5.05	14.49 14.72	$C_{31}H_{25}N_5O$		2221 2190	1615	

Firstly the formation of the zwitterion (a) by nucleophilic attack of the amine may be hypothesized; in the presence of a poor leaving group (CN), deprotonation of the ion (a) by a second amine molecule is preferred, followed by C—CN bond cleavage leading to (b) and then to the final compound. Preliminary kinetic measurements are in accord with the proposed mechanism and show a dependence of the reaction rate from the nature of the amine as reported below.

In our case an initial charge-transfer interaction can be excluded due to the fact that no transient appreciable modification is noted in the spectra on mixing the starting materials.

The cited tricyanovinyl phenylhydrazones were reacted with the amines reported in Table 1 in anhydrous dioxane until disappearance of the deeply violet colour (see Experimental). The isolated adducts **1**–**20** were characterized as reported in Table 1.

The amines were used in large excess. The reaction between benzaldehyde-*p*-(tricyanovinylidene)methylphenylhydrazone and the cited amines was also studied spectrophotometrically, following the decrease of the maximum of the tricyano derivative at 540 nm (using a mixture MeCN/CCl_4 as a solvent) until the decrease of the absorbance was significant (60–95%). The reactions showed a pseudo-first order kinetics in any case. By plotting ln C_0/C (where C_0 and C were the concentrations of the tricyanovinyl compound at zero and time t) against time (s), the rate coefficients k^1_{obs} were calculated while the second-order coefficients (k^2_{obs}) were obtained by the ratio k^1_{obs}/[Amine] (Table 2).

Table 2. *Rate coefficients*

	Piperidine	Morpholine	Pyrrolidine	Diethylamine
$\frac{[\text{Amine}]\ 10^{-1}}{M}$	3.07	60.7	3.16	3.78
K^1_{obs} sec^{-1}	2.93×10^{-3}	5.0×10^{-5}	2.9×10^{-2}	1.5×10^{-3}
K^2_{obs} mol^{-1}l sec^{-1}	1.7	1.5×10^{-3}	16.4	0.71

A large difference in rate coefficient may be noted among the reported amines as a consequence of the different nucleophilic character and relative basicity of the amines (pyrrolidine > piperidine > diethylamine > morpholine).

Kinetic measurements in the case of the reaction between *p*-anisidine and the tricyanovinyl compound are not reported owing to the low reaction rate at 20–40 °C. Our preliminary results show that k^2_{obs} increases with the amine concentration (using morpholine, for a value of [Amine] $10^{-1}/M = 60.7$ and 121.4 the corresponding values of k^2_{obs} are $1.5 \cdot 10^{-3}$

and $9 \cdot 10^{-2}$ respectively). The reactions go faster to completion with solvents characterized by a higher dielectric constant.

For the system morpholine-tricyanovinyl derivative we obtained values of k^1_{obs} $1.6 \cdot 10^{-2}$ and $6.2 \cdot 10^{-3}$ and values of k^2_{obs} $1.5 \cdot 10^{-3}$ and 0.48 for a [Amine] $10^{-1}/M$ ratio = 60.7 when the solvents were 1/2 $Me\mathrm{CN}/\mathrm{CCl}_4$ and 2/1 $Me\mathrm{CN}/\mathrm{CCl}_4$, respectively.

The reaction rate increases with the temperature: in the case of the cited system ([morpholine] = $3.4 \cdot 10^{-2}$ M and solvent $Me\mathrm{CN}/\mathrm{CCl}_4$ 1/2) we calculated a value of $k^1_{\mathrm{obs}} = 5.0 \cdot 10^{-5}$ at 20 °C and $2.5 \cdot 10^{-4}$ at 40 °C.

A comparison among IR data in Table 1 allows some considerations: (i) generally an appreciable change in νNH absorption is introduced when —CN is replaced by amine and the direction of the shift does not follow a precise trend; (ii) the νCN absorption is characterized by two distinct sharp bands, while in the starting compounds the band at lower wave numbers is a weak shoulder (as an indication of a larger difference between the two νCN groups owing to the introduction of a bulkier group on the α-vinylic carbon); (iii) the νC=N stretching vibrations are positioned at higher wavenumbers with respect to the starting compound as a consequence of a higher charge localization on the phenylhydrazono skeleton [8].

Molecular Geometry of Compound **2**

The two benzene rings are planar within the limit of accuracy [maximum out-of-plane = 0.02 (1) Å]. The angle between planes is 16.8 (1)°. The individual geometrical dimensions follow the pattern established for this type of ring being 1.382 (4), 1.384 (5) Å and 120.1 (3), 119.9 (4)° the mean bond distances and bond angles for planes C1 ... C6 and C8 ... C13 respectively.

In the hydrazine chain the double bond is mainly localized between N1 and C7 and the geometry agrees very well with that of the 1,2-benzisothiazol-3-ylhydrazone of *p*-nitrobenzaldehyde or with those of nine other fragments of C—NH—N=C found [10] in the Cambridge Data Centre Files, in which the N1—C7 bond ranges between 1.254 and 1.304 Å; N1—N2 is between 1.354 and 1.424 Å and N2—C8 between 1.331 and 1.403 Å. The N1—N2 bond [1.351 (3) Å] is intermediate between the value of 1.45 Å found for a single N—N bond in hydrazine [11] and that of 1.24 Å reported for a double N=N bond [12].

It will be noted that the two bonds formed by the N5 atom with carbons of the ring [1.468 (2), 1.469 (3) Å] are longer if compared with N5—C14 [1.340 (2) Å] which agrees well with the value of 1.340 Å found for a C—N bond in pyridine [13]. This shortening may be ascribed to a partial conjugation effect of the aromatic ring and to the triple C≡N bonds *via* a ternary C14 carbon.

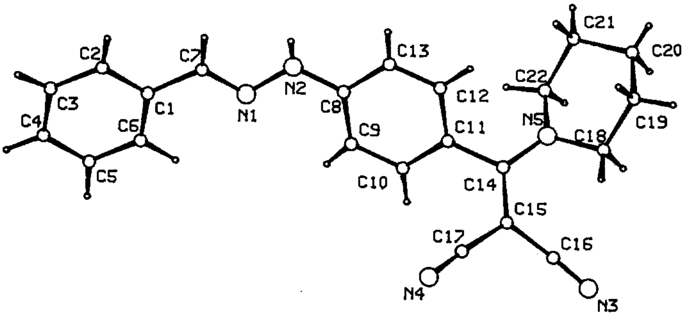

Fig. 1. Projection of the molecule with the arbitrary numbering scheme

The C—C bond lengths in the piperidine ring range from 1.503 (5) to 1.520 (4) Å with a mean value of 1.511 (4) Å; bond angles within the ring are in the range 110.3 (3)–112.7 (2)° [mean = 111.8 (3)°].

The dicyanoethylene group, which shows normal bond distances and angles, is bent by 51.4 (1) and 48.0 (1)° with respect to the mean aromatic and piperidinic ring planes, respectively.

The packing of the molecules, which is illustrated in Fig. 2, is mainly determined by *Van der Waals* forces. The shortest intermolecular bond is H1 N2 ... $N4^i$ = 2.37 (4) Å [$i = x, -y + 1/2, z + 1/2$; N2—H1 N″ ... N4 = 173.3 (33)°].

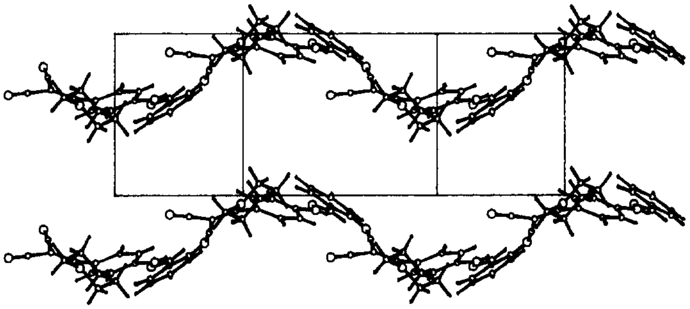

Fig. 2. Packing of the molecules along x

Experimental

UV-Vis and IR spectra were registered on Perkin-Elmer 554 and 298 instruments.

p-(Tricyanovinylidene)phenylhydrazones were prepared according to Ref. [5]. The amines were Fluka pure reagents and were purified before use. All solvents were Carlo Erba RP-ACS grade and were dried and purified according to *Vogel* [14].

Synthesis of Compounds **1–20**

Dioxane solutions of tricyanovinyl compound and amine (molar ratio 1/10) were left to stand at room temperature or were refluxed until the deeply coloured solution turned into light yellow. The mixture was cooled and reduced under vacuum to a small volume. The precipitate was collected and purified by the appropriate solvent. The yields were nearly quantitative.

Table 3. *Atomic coordinates* (× 10^4) *and thermal parameters* (× 10^4 Å^2); U (I, J) *in the form* $\exp[-2^*\mathrm{PI}^2(\mathrm{U}11^*\mathrm{H}^{2*}(\mathrm{A}^*)^2+\ldots+2\mathrm{U}12^*\mathrm{H}^*\mathrm{K}^*(\mathrm{A}^*)^*(\mathrm{B}^*)+\ldots)]$

	X/A	Y/B	Z/C	U11	U22	U33	U23	U13	U12
N1	7859(1)	584(3)	5265(1)	379(9)	1029(15)	377(8)	-5(8)	89(7)	58(9)
N2	6896(2)	894(4)	4988(1)	396(10)	1564(25)	376(9)	-118(12)	123(8)	139(12)
N3	3554(2)	1169(4)	-872(1)	631(13)	1694(27)	412(10)	-224(13)	168(10)	-228(14)
N4	6073(2)	2922(3)	1219(1)	617(12)	944(14)	485(10)	-55(9)	257(8)	-252(11)
N5	3189(1)	532(2)	1197(1)	344(8)	609(9)	399(8)	73(7)	105(6)	9(7)
C1	9476(1)	681(3)	6470(1)	415(10)	1048(17)	361(9)	-13(10)	90(7)	-19(10)
C2	10051(2)	1287(5)	7309(2)	529(13)	1643(30)	452(12)	-230(15)	130(10)	-35(16)
C3	11047(2)	1021(5)	7712(2)	531(14)	1928(37)	450(12)	-139(16)	(11)	-137(17)
C4	11488(2)	132(4)	7292(2)	423(12)	1463(26)	563(12)	85(14)	102(10)	(14)
C5	10922(2)	-428(3)	6453(2)	486(11)	996(18)	642(13)	56(12)	186(10)	34(11)
C6	9922(1)	-158(3)	6052(1)	453(10)	859(14)	484(10)	-37(10)	112(8)	-28(10)
C7	8416(2)	974(4)	6063(1)	454(12)	1256(23)	358(10)	-59(12)	128(9)	35(12)
C8	6236(1)	825(3)	4115(1)	379(10)	752(13)	366(9)	-9(9)	114(8)	7(9)
C9	6468(1)	207(3)	3468(1)	341(10)	644(12)	440(10)	15(8)	159(8)	55(8)
C10	5789(1)	225(2)	2599(1)	397(9)	551(10)	390(9)	-10(8)	174(7)	-6(8)
C11	4852(1)	832(2)	2348(1)	383(10)	534(10)	360(9)	4(7)	134(8)	-7(7)
C12	4610(1)	1408(3)	3000(1)	346(10)	657(12)	400(9)	-10(8)	133(7)	43(8)
C13	5287(2)	1411(3)	3864(1)	426(11)	815(15)	398(10)	-77(9)	191(8)	28(9)
C14	4121(1)	929(2)	1413(1)	373(9)	509(10)	374(9)	-7(7)	128(7)	11(7)
C15	4435(1)	1495(3)	804(1)	423(10)	680(12)	323(9)	-18(8)	122(7)	-44(8)
C16	3918(2)	1302(3)	-121(1)	493(12)	944(17)	382(11)	-85(10)	176(9)	-113(11)
C17	5353(2)	2282(3)	1070(1)	525(12)	744(13)	313(9)	-45(8)	175(8)	-79(10)
C18	2353(2)	1036(3)	380(1)	399(11)	802(15)	433(11)	125(10)	73(8)	7(10)
C19	1489(2)	1463(4)	552(2)	422(13)	891(18)	794(17)	213(15)	164(12)	99(12)
C20	1217(2)	179(4)	1019(2)	418(13)	1104(23)	855(19)	151(17)	267(13)	-5(13)
C21	2103(2)	-291(4)	1862(2)	488(12)	1016(20)	615(14)	128(14)	230(11)	-83(12)
C22	2940(2)	-734(3)	1659(1)	448(12)	617(12)	504(11)	122(9)	124(9)	-41(9)
H2	9762(19)	1864(34)	7566(17)	816(79)					
H3	11489(25)	1540(39)	8266(20)	1083(94)					
H4	12198(22)	-78(29)	7590(16)	848(75)					
H5	11193(20)	-1112(32)	6105(17)	896(82)					
H6	9483(22)	-493(35)	5417(18)	967(89)					
H1N2	6757(19)	1155(31)	5288(19)	559(77)					
H7	8153(20)	1617(35)	6384(18)	798(79)					
H9	7017(20)	-196(27)	3549(15)	543(61)					
H10	5954(18)	-252(29)	2190(15)	568(61)					
H12	3977(17)	1820(28)	2848(14)	527(58)					
H18B	2582(20)	1977(35)	132(18)	782(78)					
H19A	1658(24)	2461(44)	884(22)	1023(107)					
H19B	881(23)	1646(35)	14(20)	814(80)					
H20A	1071(25)	-816(40)	585(22)	945(98)					
H20B	750(33)	308(47)	1094(24)	1137(136)					
H21A	2275(21)	696(34)	2256(18)	723(76)					
H21B	1918(19)	-1264(32)	2177(16)	693(71)					
H22A	2711(20)	-1658(33)	1278(17)	725(73)					
H22B	3549(17)	-1001(24)	2151(14)	460(52)					

Table 4. *Bond distances* (Å), *bond angles* (°) *and selected torsional angles* (°)

N1 - N2	1.351(3)	C8 - C9	1.394(3)
N1 - C7	1.281(2)	C8 - C13	1.401(3)
N2 - C8	1.373(2)	C9 - C10	1.375(2)
N3 - C16	1.147(2)	C10 - C11	1.391(2)
N4 - C17	1.144(4)	C11 - C12	1.398(3)
N5 - C14	1.340(2)	C11 - C14	1.481(2)
N5 - C18	1.468(2)	C12 - C13	1.367(2)
N5 - C22	1.469(3)	C14 - C15	1.399(3)
C1 - C2	1.395(3)	C15 - C16	1.418(2)
C1 - C6	1.374(3)	C15 - C17	1.426(3)
C1 - C7	1.466(3)	C18 - C19	1.510(5)
C2 - C3	1.376(4)	C19 - C20	1.503(5)
C3 - C4	1.393(6)	C20 - C21	1.520(4)
C4 - C5	1.379(4)	C21 - C22	1.505(5)
C5 - C6	1.381(3)		

N2 - N1 - C7	115.2(2)	C10 - C11 - C14	121.9(1)
N1 - N2 - C8	121.9(2)	C10 - C11 - C12	118.6(1)
C18 - N5 - C22	113.2(2)	C12 - C11 - C14	119.4(2)
C14 - N5 - C22	121.8(2)	C11 - C12 - C13	120.7(2)
C14 - N5 - C18	123.7(2)	C8 - C13 - C12	120.7(2)
C6 - C1 - C7	122.3(1)	N5 - C14 - C11	118.7(2)
C2 - C1 - C7	118.6(2)	C11 - C14 - C15	118.0(2)
C2 - C1 - C6	119.1(2)	N5 - C14 - C15	123.3(1)
C1 - C2 - C3	120.0(3)	C14 - C15 - C17	122.1(1)
C2 - C3 - C4	120.4(3)	C14 - C15 - C16	125.0(2)
C3 - C4 - C5	119.3(3)	C16 - C15 - C17	112.9(2)
C4 - C5 - C6	119.9(2)	N3 - C16 - C15	175.7(3)
C1 - C6 - C5	121.2(2)	N4 - C17 - C15	174.9(2)
N1 - C7 - C1	121.9(2)	N5 - C18 - C19	110.5(2)
N2 - C8 - C13	118.4(2)	C18 - C19 - C20	113.3(2)
N2 - C8 - C9	123.1(2)	C19 - C20 - C21	110.3(3)
C9 - C8 - C13	118.6(1)	C20 - C21 - C22	109.7(2)
C8 - C9 - C10	120.5(2)	N5 - C22 - C21	112.7(2)
C9 - C10 - C11	120.9(1)		

N2 - N1 - C7 - C1	178.5(3)	C10 - C11 - C14 - N5	138.1(2)
C7 - N1 - N2 - C8	167.6(3)	C12 - C11 - C14 - N5	-43.9(3)
N1 - N2 - C8 - C9	10.0(4)	C10 - C11 - C14 - C15	-44.5(3)
N1 - N2 - C8 - C13	-169.7(3)	C12 - C11 - C14 - C15	133.6(2)
C18 - N5 - C22 - C21	-56.0(3)	C11 - C14 - C15 - C16	163.5(2)
C14 - N5 - C22 - C21	136.8(3)	N5 - C14 - C15 - C16	-19.2(4)
C14 - N5 - C18 - C19	-140.2(3)	C11 - C14 - C15 - C17	-13.6(3)
C22 - N5 - C14 - C11	-34.4(3)	N5 - C14 - C15 - C17	163.7(2)
C18 - N5 - C14 - C11	159.8(2)	N5 - C18 - C19 - C20	-52.9(4)
C18 - N5 - C14 - C15	-17.5(4)	C18 - C19 - C20 - C21	54.3(4)
C22 - N5 - C14 - C15	148.3(2)	C19 - C20 - C21 - C22	-54.2(4)
C22 - N5 - C18 - C19	52.9(3)	C20 - C21 - C22 - N5	55.7(3)
C6 - C1 - C7 - N1	-6.3(4)		
C2 - C1 - C7 - N1	173.3(3)		

UV-Visible Determinations

The appropriate thermostated solutions were mixed directly in the cell and the reaction was followed spectrophotometrically at 540 nm (the λmax of II) in a thermostat-controlled chamber. The pseudo-first order plots which where observed with excess of amines were linear (unless after an initial anomalous trend) giving k^1_{obs}. k^2_{obs} values were calculated by dividing k^1_{obs} by [Amine].

X-Ray of Compound **3**

Lattice parameters were obtained from least-squares fit to the angular values of 26 reflections accurately centered on the diffractometer. Intensity data were collected at room temperature on a Siemens AED single crystal diffractometer equipped with a General Automation Jumbo 220 computer using a modified [15] version of the *Lehmann & Larsen* procedure [16] in the 3–70° ϑ range. One check reflection measured every 50 reflections showed no decay in intensity. The index range was: h − 20 to 18; k 0 to 10; l 0 to 16. A total number of 3993 reflections were measured, 3754 were unique with $r_{int} = 0.011$ and 2581 of these were considered observed having $I \geqslant 2\,\sigma\,(I)$. Corrections were applied for *Lorentz* and polarisation effects while absorption was ignored.

The structure was solved by direct methods using the SHELX program [17]. The refinement was performed by bloc-matrix least-squares with non-hydrogen atoms anisotropic. All the H atoms, which were located in a ΔF map, were refined isotropically. The quantity $\sum w\,(\Delta F)^2$ was minimized and the final R value was 0.049 while R_w was 0.067 with $w = 1.0816/(\sigma^2 F + 0.04599\ F^2)$. 329 parameters were refined; the final maximum $\Delta\rho$ was 0.17 eA^{-3} while the final maximum Δ/σ was 0.39.

Crystal data: $C_{22}H_{21}N_5$, $M = 355.4$, monoclinic, space group = $P2_1/c$; $a = 15.206(2)$, $b = 8.430(2)$, $c = 16.954(3)$ Å; $\beta = 116.29(3)°$, $V = 1948.5$ Å^3; $Z = 4$; $D_c = 1.21$ g/cm^3; $F(000) = 752$; CuK_α radiation, $\bar{\lambda} = 1.5418$ Å; $\mu = 5.53$ cm^{-1}.

Atomic scattering factors were those of SHELX. The atomic final coordinates of the molecule, illustrated in Fig. 1, are listed in Table 3. Table 4 reports bond distances, bond angles and selected torsional angles.

All the computations were performed on a Gould Sel 32/77 computer. Lists of structure factors amplitudes are available from one of the authors (*G. B.*) on request.

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