and Sabouraud's agar for the fungal tests. All bacterial cultures were incubated at 35° and the fungal cultures at room temperature. The filter paper disks (12.7-mm. diameter) were saturated with 0.1 ml. of a 1:1000 concentration of the compounds to be tested; the solvent was allowed to evaporate before the disks were placed, in duplicate, on the seeded plates. Ethanolic solutions of eight of the compounds were used. The other compound [*m*-(2-nitrovinyl)-phenyl acetate] was employed as a suspension in pyridine. Disks impregnated with an equal amount of the solvent only were dried and used as controls and in no instance exhibited any inhibition. The zones of inhibition were read at the end of 24 hr. of incubation for the bacteria and 48 hr. for the fungi. The results are tabulated in Table I.

DISCUSSION

Nine β-nitrostyrene derivatives were tested by the paper disk method for antimicrobial activity. Of the six 3-nitro-4-substituted phenoxy-β-nitrostyrenes tested, the parent compound had the widest spectrum. The pentachloro derivative was effective against *S. aureus* only, and the pentabromo derivative was inactive. None of these compounds had any activity against *P. vulgaris* or *P. aeruginosa*.

The three ring-substituted β-nitrostyrenes tested all showed good activity against the test organisms. Of particular significance is their activity against the *Proteus* and *Pseudomonas* species tested. One limitation with the most active compound tested, *m*-acetoxy-β-nitrostyrene, was the inability to solubilize it in common organic solvents, even at a 1:1000 concentration. It was placed on the paper disk as a 1:1000 suspension. The results of the tests of the latter series of compounds warrant further study of other derivatives of this group.

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Solvent Effects in the NMR Spectra of Cyano Compounds

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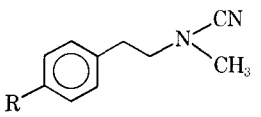
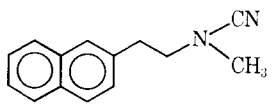
Abstract □ Novel solvent effects in the NMR spectra of certain cyano compounds are reported. A change in the splitting pattern of the methylene groups of *N*-cyano-*N*-methylarylethylamines with a change in solvent was observed in open-chain alkyl cyano compounds containing a terminal aromatic ring.

Keyphrases □ Solvent effects—NMR spectra, cyano compounds □ Cyano compounds, NMR—solvent effects □ NMR spectra—solvent effects, cyano compounds

During the synthesis of a number of *N*-cyano-*N*-methylarylethylamines (1), it was observed that the NMR spectra exhibited dramatic changes when the solvent was changed from either carbon tetrachloride or deuterochloroform to benzene. These changes involved: (*a*) a strong upfield shift in the singlet signal due to the *N*-methyl protons, and (*b*) a strong upfield shift of the multiplets due to the four methylene protons, accompanied by a pronounced change in the splitting pattern of the multiplet in all of the compounds where rotation was possible about the C—C bond of the ethylamine. The only compound examined which did not show the change in splitting pattern was *N*-cyanotetrahydroisoquinoline (Compound 5). The observations from the examined spectra are summarized in Table I.



1. R = H
2. R = OCH_3



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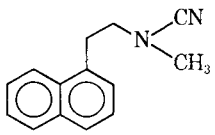

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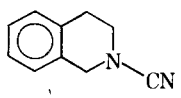

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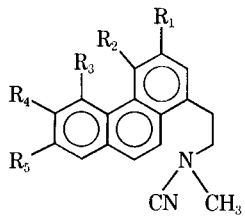
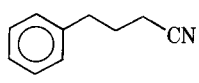


	R_1	R_2	R_3	R_4	R_5
6.	—OCH_2O—		OH	OMe	H
7.	—OCH_2O—		OAc	OMe	H
8.	H	H	OH	OH	H
9.	OH	OMe	H	OMe	OH



10

$ClCH_2CH_2CN$

11

$BrCH_2CH_2CH_2CN$

12

structures of compounds listed in Table I

Table I—Solvent Effects on Chemical Shifts in the NMR of Cyano Compounds

Compound	Solvent	Chemical Shift (δ) N—CH_3	Chemical Shift (δ) —CH_2—CH_2—
1	CCl_4	2.66	Multiplet; 2.66–3.29
1	C_6H_6	2.00	Multiplet as singlet; 2.47
2	$CDCl_3$	2.87	Multiplet; 2.87–3.51
2	C_6H_6	2.12	Multiplet as singlet; 2.57
3	$CDCl_3$	2.80	Multiplet; 3.07–3.39
3	C_6H_6	2.07	Multiplet as singlet; 2.67
4	$CDCl_3$	2.78	Multiplet as singlet; 3.37
4	C_6H_6	2.05	Multiplet; 2.47–3.26
5	CCl_4	4.30($NCH_2\phi$)	Irregular triplet; 2.88 ($W_{1/2}$ = 13 c.p.s.) Irregular triplet; 3.41 ($W_{1/2}$ = 13 c.p.s.)
5	C_6H_6	3.44($NCH_2\phi$)	Irregular triplet; 1.93 ($W_{1/2}$ = 13 c.p.s.) Irregular triplet; 2.41 ($W_{1/2}$ = 13 c.p.s.)
6	$CDCl_3$	2.80	Multiplets as singlet; 3.27
6	$CDCl_3$–C_6H_6(2:1)	2.38	Multiplet; 2.86–3.17
7	$CDCl_3$	2.81	Multiplet as singlet; 3.31
7	$CDCl_3$–C_6H_6(1:1)	2.12	Multiplet; 2.40–3.18
8	$CDCl_3$	2.83	Multiplet as singlet; 3.42
9	$CDCl_3$	2.90	Multiplet as singlet; 3.41
10	CCl_4		Irregular triplet; 2.77 ($W_{1/2}$ = 14 c.p.s.) Multiplet; 1.33–1.84
10	C_6H_6		Irregular triplet; 3.26 ($W_{1/2}$ = 14 c.p.s.) Multiplet; 2.00–2.92
11	CCl_4		Triplet; 3.73 (J = 6.5 c.p.s.) Triplet; 2.83 (J = 6.5 c.p.s.)
11	C_6H_6		Triplet; 2.88 (J = 6.5 c.p.s.) Triplet; 1.88 (J = 6.5 c.p.s.)
12	CCl_4		Triplet; 3.51 (J = 6 c.p.s.) Multiplet; 1.99–2.70
12	C_6H_6		Triplet; 2.79 (J = 6 c.p.s.) Multiplet; 1.14–1.84

There appears to be no long-range coupling effects between the methylene protons and the protons of the aromatic ring in any of these arylethylamines. Decoupling experiments were performed on Compounds 1, 3, and 4 by irradiating the aromatic region of the spectra. This had no effect on the splitting pattern of the methylene groups when either deuterochloroform or benzene was utilized as the solvent.

The NMR spectrum of phenylbutyronitrile (Compound 10) exhibited equally strong solvent effects, involving upfield shifts accompanied by pronounced changes in the patterns of the methylene signals. The spectra of the alkyl cyano compounds β-chloropropionitrile (Compound 11) and γ-bromobutyronitrile (Compound 12) exhibited upfield shifts of equal magnitude with no change in the splitting pattern, whereas *N,N*-dimethylphenethylamines showed no significant solvent effects in their NMR spectra.

These solvent effects, therefore, appear to be due to the cyano group and can be explained on the basis of a collision complex between the benzene ring and the cyano group. Similar collision complexes have been postulated by Hatton and Richards (2) and have been applied to explain the solvent effects caused by benzene with *N*-methyl formamide (3) and several ketones (4, 5). The general upfield shifts in the case of the nonaromatic protons can be attributed to the anisotropy of the magnetic susceptibility of benzene. The change in the splitting pattern of the methylene peaks, which is observed with all of the open-chain alkyl cyano compounds containing a terminal aromatic ring (Compounds 1–4, 6, 7, 10), can be attributed to: (*a*) a decrease in the shielding effect of benzene when the methylene groups are further removed from the cyano group, and (*b*) conformational changes accompanying the change in solvent.

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