NMR Spectral Parameters for Some o-Disubstituted Benzenes

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The NMR spectral parameters for a diverse series of o-disubstituted benzenes have been determined both at 60 and 100 Mc. in dilute solutions of carbon tetrachloride.

RECENTLY, the authors measured the NMR spectral parameters of a series of *o*-disubstituted benzenes (*3*), and continuing the original work, a number of further examples have been examined. Since the number of reported spectra for unsymmetrical four spin systems is limited and the parameters for these compounds have been determined at both 60 and 100 Mc., several of these spectra have been reproduced to aid others (Figures 1 to 4). The determined parameters are given in Table I, and the mode of calculation and assignment in the Experimental section. A detailed discussion of these data and the current theory of chemical shifts will appear elsewhere (*4*).

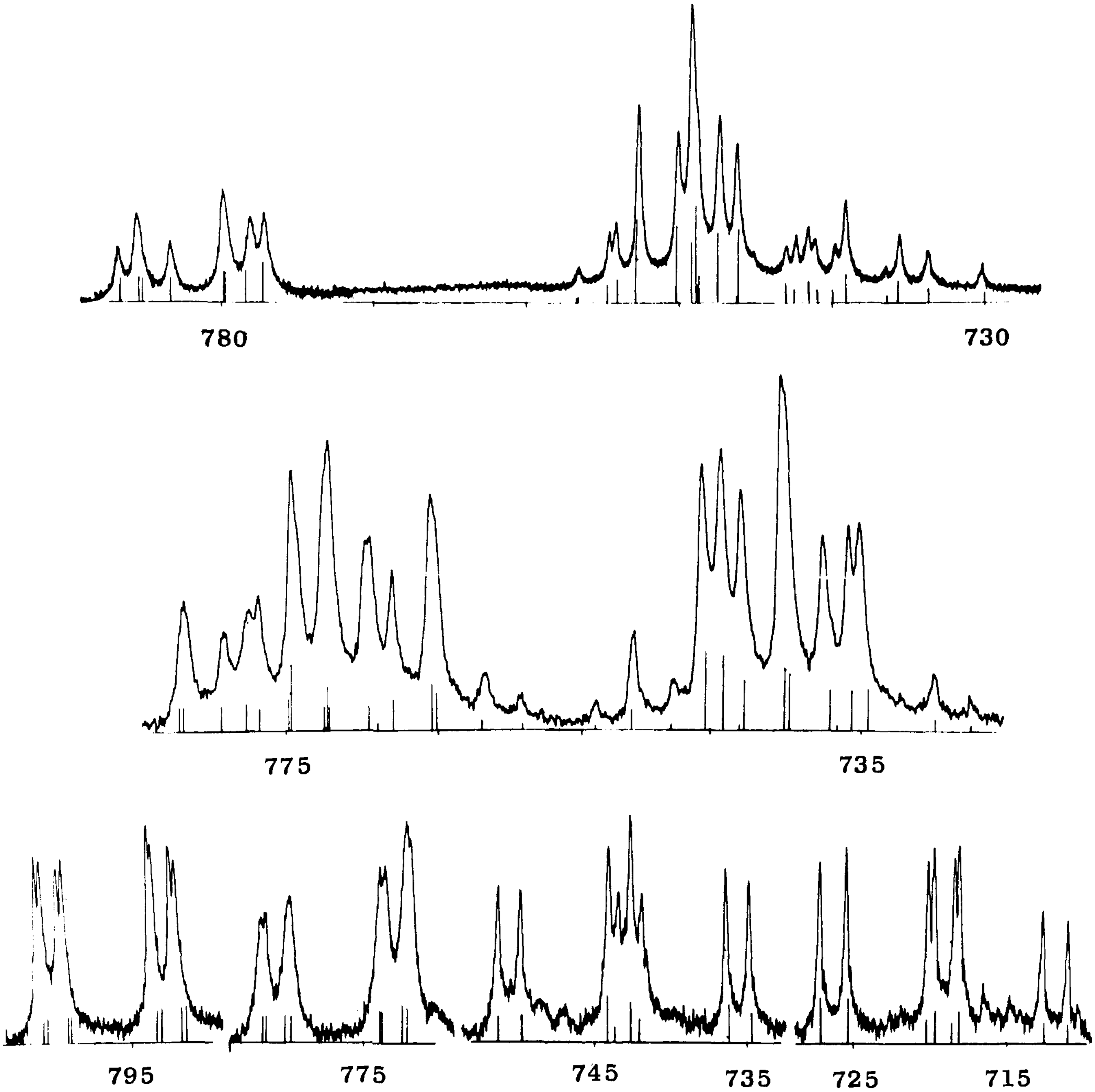

Figure 1. NMR spectra (100 Mc.) of 1-chloro-2-nitrobenzene (top), 1-bromo-2-nitrobenzene (middle), and 1-iodo-2-nitrobenzene (bottom)

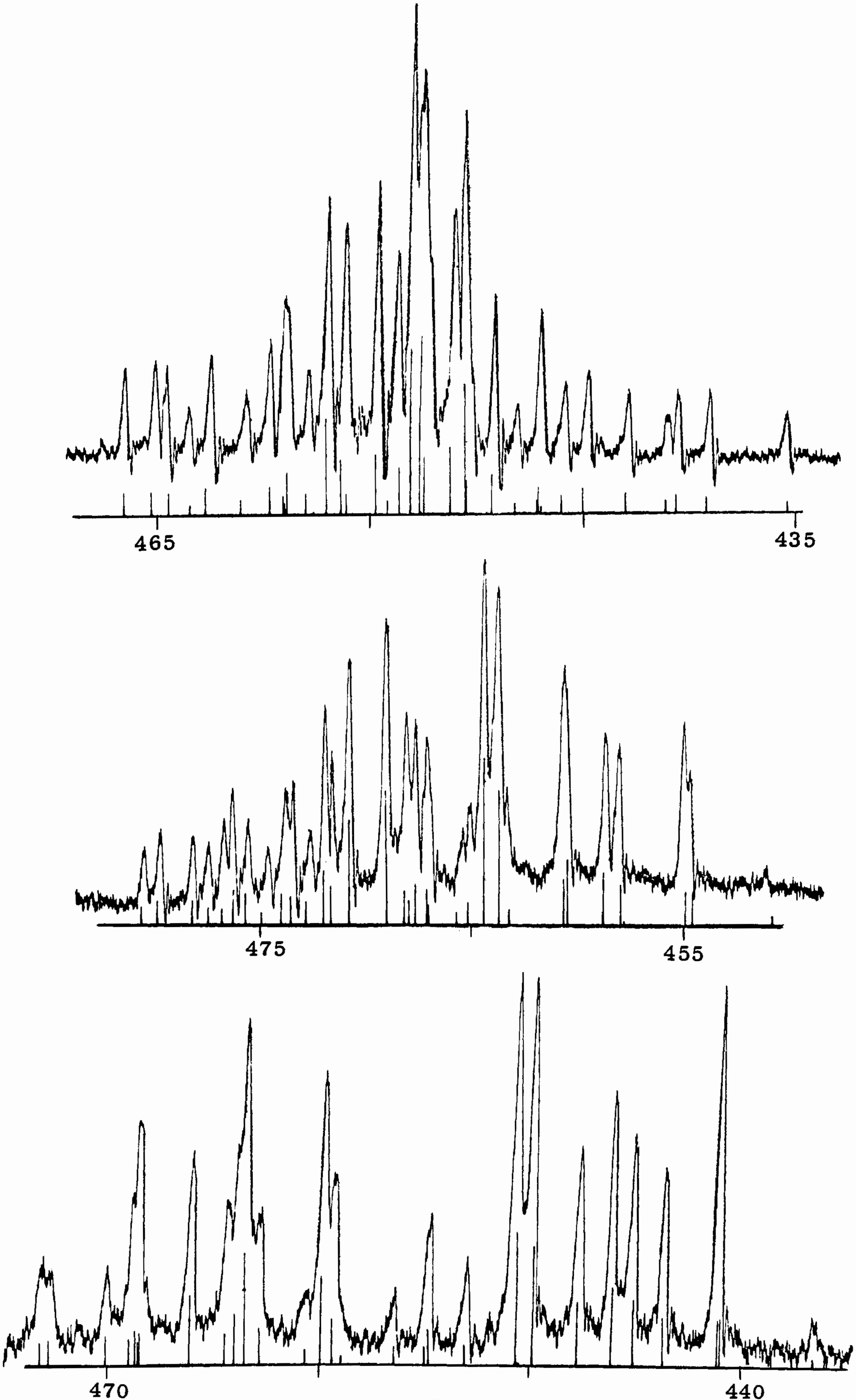

Figure 2. NMR spectra (60 Mc.) of 1-chloro-2-cyanobenzene (top), 1-bromo-2-cyanobenzene (middle), 1-bromo-2-nitrobenzene (bottom)

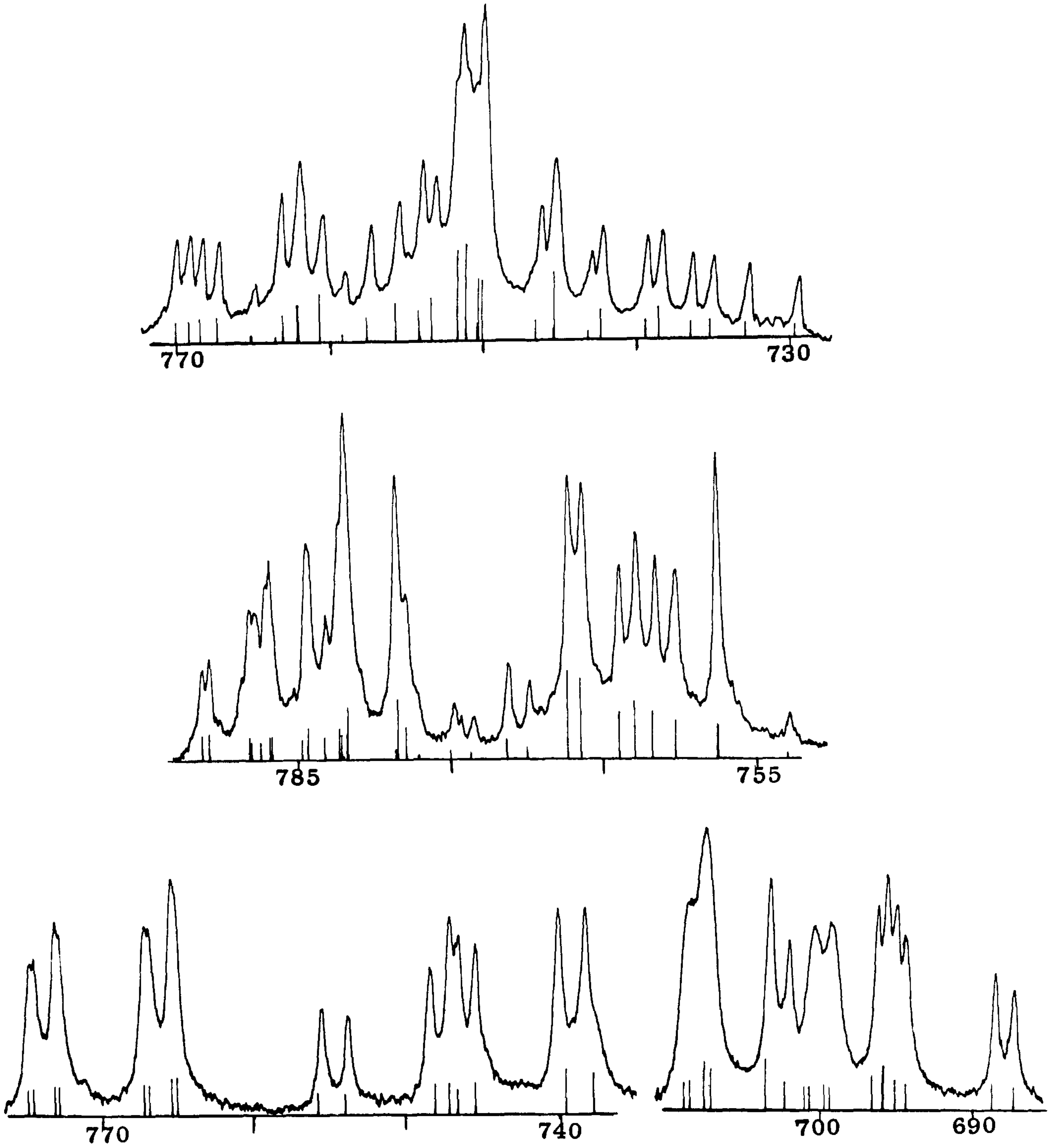

Figure 3. NMR spectra (100 Mc.) of 1-chloro-2-cyanobenzene (top), 1-bromo-2-cyanobenzene (middle), and 1-methoxy-2-nitrobenzene (bottom)

EXPERIMENTAL

The compounds used in this study were all commercially available. Samples were prepared as *ca.* 10% solutions in carbon tetrachloride containing *ca.* 5% tetramethylsilane as an internal standard. All were vacuum degassed and sealed.

All spectra were determined at both 60 and 100 Mc. on Varian instruments operating at ambient temperatures (*ca.* 40° C.) and at resolutions of 0.2 to 0.3 cycle per second. Each spectrum was recorded four to six times and the line positions averaged.

Spectral analysis of the unsymmetrical compounds followed the principles laid down previously (*3*). Refinement was carried out with the aid of the Laocoon II program (*1*). Root mean square deviation between calculated and experimental line frequencies were typically 0.03 to 0.1 cycle per second.

The chemical shifts and coupling constants from these spectra are given in Table I. The chemical shifts for protons not adjacent to substituents were assigned by consideration of the values predicted by the parameters of Martin and Dailey (*2*). Adjacent protons were then assigned from the splitting patterns. For tightly coupled spectra, such as the

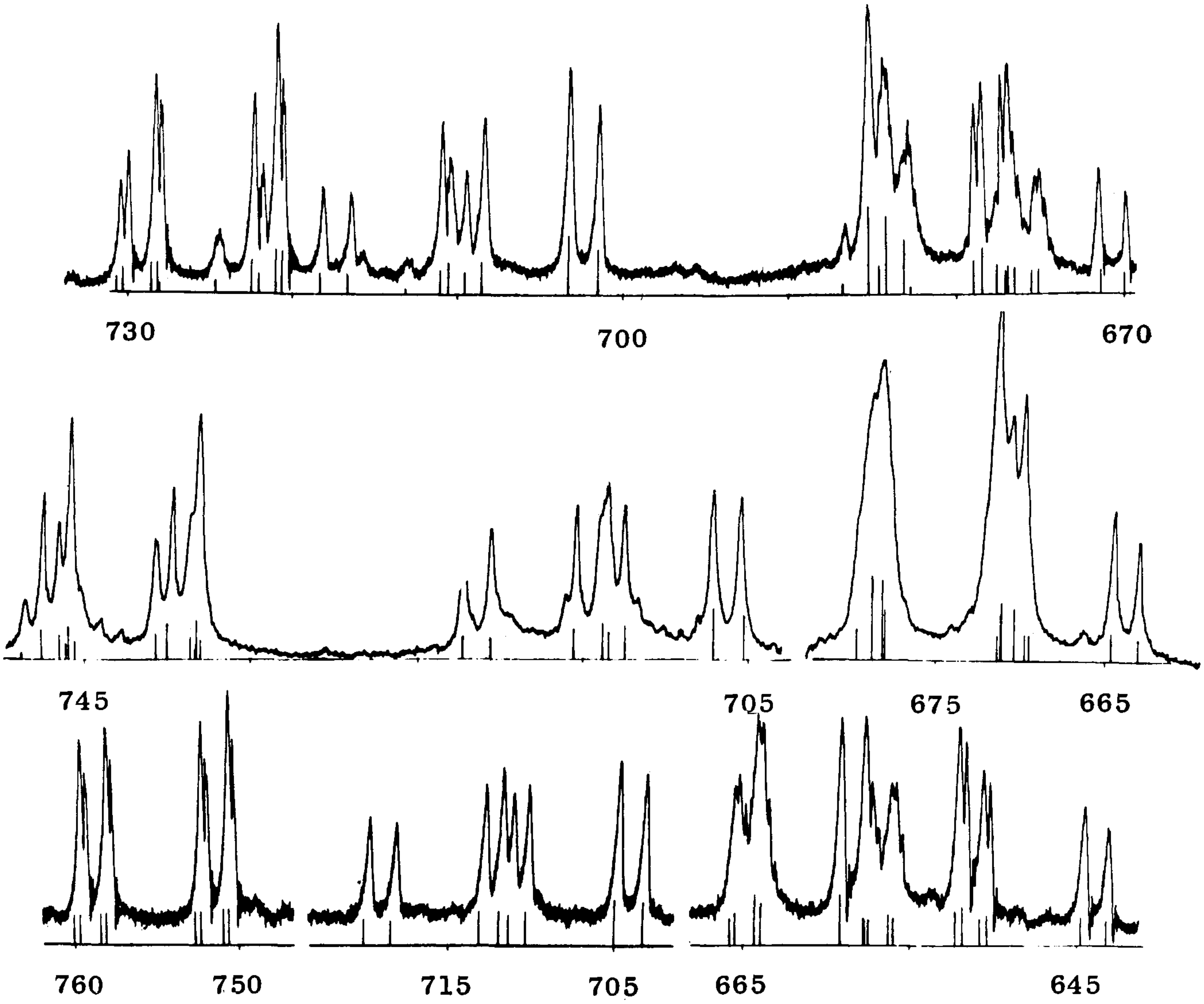

Figure 4. NMR spectra (100 Mc.) of 2-methoxy-1-chlorobenzene (top), 2-methoxy-1-bromobenzene (middle), and 2-methoxy-1-iodobenzene (bottom)

Table I. NMR Parameters for Disubstituted Benzenes[a]

Benzenes	J_{34}	J_{45}	J_{56}	J_{35}	J_{46}	J_{36}	γ_3	γ_4	γ_5	γ_6
1-Chloro-2-methoxy	7.9_9	7.3_0	7.7[illegible]	1.1_9	1.6_2	0.3_1	3.19 (3.28)	2.90 (3.00)	3.20 (3.21)	2.74 (2.84)
1-Bromo-2-methoxy	8.3_1	7.6_3	7.8_0	1.5_4	1.6_3	0.1_9	3.23 (3.34)	2.85 (2.91)	3.27 (3.27)	2.56 (2.68)
1-Iodo-2-methoxy	8.0_5	7.1_7	7.5_5	1.3_8	1.6_2	0.2_9	3.29 (3.48)	2.80 (2.91)	3.39 (3.40)	2.31 (2.48)
1,2-Dimethoxy	...	...	...	...	...	...	3.25 (3.32)	3.25 (3.25)	3.25 (3.25)	3.25 (3.32)
1-Chloro-2-nitro	8.2_3	7.1_3	7.6_7	1.1_7	1.4_1	0.7_8	2.18 (1.84)	2.59 (2.63)	2.51 (2.51)	2.46 (2.57)
1-Bromo-2-nitro	7.8_6	7.5_3	8.2_7	1.6_6	1.2_2	0.1_9	2.22 (1.90)	2.56 (2.64)	2.60 (2.57)	2.29 (2.41)
1-Iodo-2-nitro	7.9_0	7.2_0	7.7_1	1.3_5	1.4_5	0.2_8	2.20 (2.04)	2.64 (2.64)	2.71 (2.71)	2.01 (2.21)
1,2-Dinitro	...	...	...	...	...	...	2.03 (1.61)	2.13 (2.28)	2.13 (2.28)	2.03 (1.61)
1-Chloro-2-cyano	7.5_2	7.5_8	8.0_8	1.4_8	0.9_5	0.4_6	2.36 (2.53)	2.62 (2.72)	2.47 (2.47)	2.50 (2.58)
1-Bromo-2-cyano	7.7_8	7.4_4	7.8_4	1.3_3	1.5_9	0.4_3	2.37 (2.59)	2.57 (2.65)	2.55 (2.53)	2.33 (2.42)
1,2-Dicyano	...	...	...	...	...	...	2.19 (2.31)	2.25 (2.25)	2.25 (2.25)	2.19 (2.31)
1-Nitro-2-methoxy	8.5_4	7.9_1	7.8_5	1.2_1	1.7_6	0.2_7	2.94 (3.05)	2.54 (2.55)	3.04 (2.98)	2.30 (1.88)

[a] Coupling constants in cycles per second; chemical shifts in τ. Values in parentheses are predicted from the values of Martin and Dailey (*2*).

chlorocyano- and bromocyanobenzenes, this procedure was not completely clear-cut, and assignment was made so as to give the most consistent results with the remainder of the data in Table I and earlier work (*3*).

Chemical shifts were also determined for 1,2-dimethoxybenzene (a single line in carbon tetrachloride), 1,2-dinitrobenzene, and 1,2-dicyanobenzene. The latter two gave typical AA′BB′ spectra, which were analyzed only for chemical shifts by oft published procedures. The results are given also in Table I.

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LITERATURE CITED

(1) Castellano, S., Bothner-By, A.A., *J. Chem. Phys.* **41**, 3863 (1964).
(2) Martin, J.S., Dailey, B.P., *Ibid.*, **39**, 1722 (1963).
(3) Smith, W.B., Cole, G.M., *J. Phys. Chem.* **69**, 4413 (1965).
(4) Smith, W.B., Roark, J.L., *J. Am. Chem. Soc.* **89**, 5018 (1967).

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Vapor-Liquid Equilibria of Binary Systems Containing Alcohols

Methanol with Aliphatic Amines

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Vapor-liquid equilibrium data are reported for three binary systems of methanol with *n*-butylamine ($BuNH_2$), diethylamine (Et_2NH), and triethylamine (Et_3N) at 730 mm. of Hg. As expected from a strong hydrogen-bond interaction between hydroxyl group and amino bases, both the methanol-$BuNH_2$ and methanol-Et_2NH systems show negative deviation from Raoult's law. However, the methanol-Et_3N system shows a positive deviation and no azeotrope can be found. Et_2NH forms an azeotropic mixture at 67.2° C. near 76.0 mole % of methanol, while a tangent azeotrope seems to occur in methanol-$BuNH_2$.

VAPOR-LIQUID equilibrium data of alcohol-amine systems are of theoretical and practical importance. A review of the literature indicates that no isobaric equilibrium data are available for binary systems of methanol with aliphatic amines, except for some information on the azeotropic behavior (*5*). This paper deals with the isobaric vapor-liquid equilibrium data of three binary systems of methanol with *n*-butylamine, diethylamine, and triethylamine.

EXPERIMENTAL

The sample liquids used in this study were prepared by the procedure described in the previous paper (*8*). Table I lists some physical properties of the final purified samples

Table I. Physical Properties of Purified Liquids and the Antoine Constants Used

	Methanol	$BuNH_2$	Et_2NH	Et_3N
Boiling point, *t*, ° C.				
Obsd.	64.8	78.0	55.4	89.4
Lit.[a]	64.5 ~ 7	77.8	55.5	89.5
Density, d^4_{25}				
Obsd.	0.78653	0.73514	0.69893	0.72353
Lit.[a]	0.7866	0.7369	0.6926	0.7235
Refractive index, n^{25}_D				
Obsd.	1.3265	1.3972	1.3824	1.3979
Lit.[a]	1.3267	1.4004	1.3783	1.3980
Antoine constants[a,b]				
A	8.07246	7.2130	7.14099	7.18658
B	1574.99	1308.4	1209.9	1341.3
C	238.86	224.2	229.0	222.0

[a] Reference (*3*). [b] Reference (*6*).

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