where subscript 1 refers to methanol. For the methanol-diethylamine system, the three-constant Margules equation derived from the general expression for the excess free energy of mixing (*10*) was used. If we denote the third constant, in addition to two constants, MA and MB in Equation 2, as MC, the equation can be written as

$$\left.\begin{aligned} \log \gamma_1 &= x_2^2[MA - 2(MA - MB + MC)x_1 + 3MC(x_1)^2] \\ \log \gamma_2 &= x_1^2[MB - 2(MB - MA + MC)x_2 + 3MC(x_2)^2] \end{aligned}\right\} \qquad (3)$$

A set of the Margules constants was evaluated from the data and tabulated in Table III. The sum of square of the deviation of calculated γ value from experimental one is given in the same table. The experimental and calculated γ values by Equation 2 or Equation 3 (for methanol-diethylamine system) are plotted in Figure 4. The correlation is especially satisfactory for the methanol-diethylamine system.

CONCLUSIONS

The present data indicate that the negative deviation from the ideal solution law are observed for the methanol-*n*-butylamine and methanol-diethylamine systems and that the methanol-triethylamine system shows, contrary to our expectation, a positive deviation which seems to be attributed to a sort of steric interference. These results are in harmony with those reported by Copp (*1*, *2*).

NOMENCLATURE

MA, MB, MC = Margules constants
p = vapor pressure, mm. of Hg
x, y = composition of liquid and vapor, mole fraction, respectively
γ = activity coefficients
π = total pressure, mm. of Hg

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Proton Magnetic Resonance Spectra of Malonate Esters

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The NMR spectra of a number of open chain and cyclic malonic esters have been measured and the characteristic resonances for the various protons in such molecules established.

IN CONNECTION with our studies on the stereochemistry of the addition of diethyl malonate to 4-*tert*-butyl-1-cyanocyclohexene (*5*) it was important to make assignments to individual protons in the NMR spectra of the malonate esters obtained. Until that time, there were no reported studies on the NMR spectra of malonate esters, but since then the spectra of diethyl malonate (*11*) and of esters of alkoxymethyl ethylmalonic acids (*10*) have been described. The spectra of some acyclic and cyclic malonate esters are now discussed.

EXPERIMENTAL

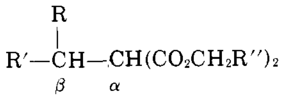
Most of the esters were commercially available and were purified before use. Diethyl ethyldeuteromalonate was prepared from the sodium salt of the ester (*1*), diethyl cyclohexylmalonate was made using the method of Hope and Perkin (*7*), and dimethyl 3-α-cholestanylmalonate and dimethyl 3-β-cholest-5-enylmalonate were obtained from the corresponding tosylates and sodiomalonic ester (*9*). Isopropylidene ethylmalonate and isopropylidene dimethylmalonate were available from a previous study (*2*). Diethyl β-cyanoethylmalonate (*6*) and diethyl 2-cyanopropylmalonate (*4*) were prepared by standard cyanoethylation reactions.

The NMR spectra were measured on a Varian A 60 instrument, tetramethylsilane being the internal standard, and CCl_4 was used as solvent except as specified. The results are summarized in Tables I and II in which only characteristic peaks are listed.

RESULTS AND DISCUSSION

The assignments for the ester CH_2 groups and for the α-CH groups are, in most cases, clear-cut. The former give rise to a 4H quartet, usually around 5.85 τ(J = 7 c.p.s.). As expected, methyl esters absorb at a somewhat higher field. The doublet observed for dimethyl 3-β-cholest-5-enylmalonate is probably due to the two ester functions in the equatorial malonate being in different magnetic environments, one of them coming under the influence of the anisotropic effect of the olefinic double bond. The slight

Table I. Characteristic NMR Lines for Open Chain Malonic Esters in CCl_4



$$\overset{\displaystyle R}{\underset{\beta}{R'-CH}}-\underset{\alpha}{CH}(CO_2CH_2R'')_2$$

Compound	Ester CH_2 quartet	τ	
		α-proton	β-protons
Diethyl malonate	5.84	6.78 (singlet)	
Diethyl methylmalonate	5.84	6.71 (1 H quartet; $J = 7$ c.p.s.)	8.65 (3 H doublet; $J = 7$ c.p.s.)
Diethyl ethylmalonate	5.84	6.91 (1 H triplet; $J = 7$ c.p.s.)	8.18 (2 H, octet)
Diethyl *n*-butylmalonate	5.85	6.83 (1 H triplet; $J = 7$ c.p.s.)	8.11 (2 H, sextet)
Diethyl diethylmalonate	5.86		8.15 (overlapping 2 H quartets)
Diethyl ethyldeuteromalonate	5.86		8.13 (overlapping 2 H quartets, or octet)
Diethyl ethylphenylmalonate	5.83		7.73 (2 H quartet, $J = 7$ c.p.s.)
Diethyl β-cyanoethylmalonate	5.79	6.59 (1 H triplet; $J = 7$ c.p.s.)	7.78 (approx.) (complex sextet overlapping with lines for γ-CH_2 at *ca.* 7.52τ).
Diethyl 2-cyanopropylmalonate	5.79	6.52 (1 H triplet; $J = 7$ c.p.s.)	7.92 (2 H broad triplet owing to slight splitting with γ-CH which appears at 7.32 τ as a broad multiplet)
Diethylcyclohexylmalonate	5.85	6.88 (1 H doublet; $J = 8$ c.p.s.)	7.85 (1 H, broad multiplet)
Dimethyl 3-α-cholestanyl-	6.29 (6 H methyl singlet)	6.38 (1 H doublet; $J = 6$ c.p.s.)	7.5 (1 H, very broad multiplet)
Dimethyl 3-β-chlolest-5-enylmalonate	6.21, 6.27 (two CH_3 singlets)	6.90 (1 H broad)	7.83 (inflexion on side of a broad peak)

Table II. Proton Magnetic Resonance Spectra of Some Cyclic Malonate Esters in $CDCl_3$ Solution

Compound	Ester CH_2	τ	
		α-proton	β-protons
Isopropylidene ethylmalonate		6.47 (1 H triplet; $J = 5$ c.p.s.)	7.82 (2 H octet)
Isopropylidene dimethylmalonate			8.29 (6 H singlet) (ester CH_3 groups, 6 H singlet at 8.42 τ)
Diethyl ethylmalonate[a]	5.78 (4 H quartet)	6.75 (1 H triplet)	9.03 (2 H octet)

[a] For comparison with open chain malonates in $CDCl_3$ solution.

deshielding of the ester CH_2 by the cyano group is seen in diethyl β-cyanoethylmalonate and diethyl 2-cyanopropylmalonate, and in *cis*-4-*tert*-butyl-1-cyano-2-cyclohexylmalonate, but not in the trans isomer (5).

The resonance due to the α-proton may be assigned unambiguously on the basis of its intensity and multiplicity, as well as by its absence in the spectra of the esters of diethyl-, ethyldeutero-, and ethylphenylmalonic acids. That it appears at higher field than the ester CH_2 protons is understandable since the well-known acidity of the α-protons is due not only to the lowering of the electron density by the ester groups but also to the resonance stabilization of the anion formed on treatment with base; only the former effect would be reflected in the NMR spectrum of the ester itself. No enol form was detected in any of the compounds studied, in agreement with the infrared spectral results (*1*).

In the only compound studied which had an axial malonate grouping in a cyclohexane ring (dimethyl 3-α-cholestanylmalonate) both the α- and the β-(equatorial) protons (of the malonic ester) absorbed at lower fields than in the other compounds examined and than the corresponding ones in diethyl cyclohexylmalonate in which the malonate group must exist predominantly in the equatorial conformation. The assignments of these β-proton lines are also reasonably straightforward, the multiplicities in all cases being as expected. On the basis of Shoolery's rules (*8*) such protons are expected to absorb at roughly 8.35τ, in reasonable agreement with the values found. The presence of a cyano group on an adjacent carbon produces the expected shift to lower field; the β-protons in diethyl ethylphenylmalonate also absorb at a lower field than usual (7.73τ). This could be due either to the inductive effect of the phenyl group or to deshielding by the ring current. The β-protons in diethyl diethylmalonate and diethyl ethyldeuteromalonate gave rise to overlapping quartets or octets. In the first case, this could be due either to the two protons being nonequivalent in each α-ethyl group (*AB* pattern) or to the two ethyl groups being in different magnetic environments owing to rotational isomerism in the malonate ester grouping (*3*). The latter alternative is not available to the deuterated compound; however, there is the possibility of a weak coupling ($J \leq 1$ c.p.s.) of the β-CH_2 protons with the α-deuterium atom. In the cyano-substituted compounds there is appreciable overlap between the absorptions owing to $-C\underline{H}-CN$ and those of the β-protons, as already noted with cyclohexane cyanomalonates (*5*).

The spectra of the two cyclic malonates studied here had to be determined in $CDCl_3$ owing to their insolubility in CCl_4. The spectrum of the parent ester (Meldrum's acid) could not be determined owing to the insolubility in the common solvents available. The α- and β-protons in these esters absorb at lower fields than do those in the corresponding open chain compounds, and this is not due to a solvent effect (Table II). Only one β-proton signal was observed for both the axial and equatorial CH_3 groups in isopropylidene dimethylmalonates, indicating rapid chair-chair interconversion of the six-membered ring. Another, but less likely, explanation could be that the ring is almost planar in these compounds. Again, no evidence of enolization was discernible in isopropylidene ethylmalonate, in agreement with the conclusions reached on the basis of the infrared spectra of Meldrum's acid and its derivatives (*2*).

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Dianils of *o*-Hydroxyaldehydes as Potential Photochromes

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Several diamine-aldehyde anils have been prepared and examined for crystalline photochromism.

A NUMBER of crystalline anils of *o*-hydroxy aromatic aldehydes have been reported to be photochromic (*2*). This photochromism has been ascribed to a topochemical phenomenon determined by the packing of the anil molecules in the crystal lattice which permits or inhibits internal photohydrogen transfer to a colored enol (*1*). Since very few of the larger molecular species, typified by symmetrical dianils, have been examined for crystalline photochromism, the authors have prepared the following diamine-aldehyde anils and investigated them in this regard. None of these compounds gave evidence of visually detectable photochromism.

Table I. Diamine-Aldehyde Anils

Amine	Aldehyde	Formula	Yield, %	M.P., ° C.	Analysis, % *N* Calcd.	Analysis, % *N* Found
1,4-Cyclohexanebis (methylamine)	2-Hydroxy-3-methoxybenzaldehyde	$C_{24}H_{30}N_2O_4$	76	153–155	6.82	6.86
	2-Hydroxybenzaldehyde	$C_{22}H_{26}N_2O_2$	45	109	7.99	7.92
	2-Hydroxy-1-naphthaldehyde	$C_{30}H_{30}N_2O_2$	65	203–204	6.21	6.21
4,4′-Diaminodiphenylmethane	2-Hydroxy-3-methoxybenzaldehyde	$C_{29}H_{26}N_2O_4$	70	192	6.00	6.06
	2-Hydroxybenzaldehyde	$C_{27}H_{22}N_2O_2$	70	214–215	6.89	6.90
Diethylenetriamine	2-Hydroxy-1-naphthaldehyde	$C_{26}H_{25}N_3O_2$	73	153–154	10.21	10.25
Ethylenediamine	2-Hydroxy-3-methoxybenzaldehyde	$C_{18}H_{20}N_2O_4$	70	161–162	8.53	8.20
p-Phenylenediamine	2-Hydroxybenzaldehyde	$C_{20}H_{16}N_2O_2$	94	212–213^a	8.86	8.80

^{a} Although this compound has been previously reported (*3*), it was synthesized for inclusion in this photochemical study.

EXPERIMENTAL

The anils employed in this study were prepared by refluxing a 0.20 to 0.10 mole ratio of the aldehyde to the diamine in 350 ml. of anhydrous methanol for 4 hours. The solvent was removed in vacuo and the product recrystallized from methanol to analytical purity. Yields and melting points are reported in Table I.

The dianils were irradiated as crystalline films on the walls of fused quartz vessels positioned 4 cm. from a Hanovia No. 30620 mercury vapor lamp. Because photochromism can sometimes be eradicated by light absorbed in the region of the new visible band (*1*), the dianils were also irradiated through a black Corning Filter No. 5860 (ultraviolet transmitting, visible absorbing).

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