4310). In 0.01 M NaOH λ_{max} was 268 mμ and λ_{min} was 252 mμ On acidification of the alkaline solution λ_{max} was 282 mμ and λ_{min} was 251 mμ. The pK_a was 1.46. On titration of the compound with alkali drifting to lower pH was observed, and upon back-titration of this solution a pK_a of 2.45 was found.

Registry No.—**2**, 10299-76-0; **3**, 10380-93-5; **4**, 10299-77-1; 2′,3′-O-isopropylidene-3,5′-cycloadenosine iodide, 10299-78-2.

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Relative Stabilities of Copper Chelates of 2-Acetylcyclanones[1]

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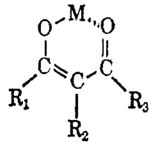
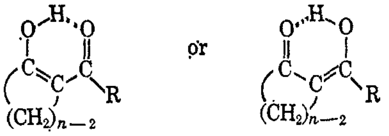
The stabilities of metal chelates of 1,3-diketones **1**, as expressed by the strengths of the oxygen-metal bonds as well as by stability constants,[3,4] are noticeably affected by electronic effects of the substituents R_1, R_2, and R_3. At the same time, the enolic character of 2



1

and many other properties of cyclic systems are distinctly altered by strain (bond angle, torsional, and transannular) within the alicyclic ring.[5] It was of interest, therefore, to see if the stabilities of the copper chelates of the enols 2 are also dependent upon the sizes of the alicyclic rings.

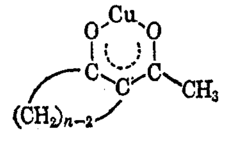


2

The C=C and Cu-O bond infrared absorption frequencies of chelates **5-15**, Table I appears in Table II. If the Cu-O bond frequencies are taken as a measure of chelate stability,[3] there is observed an alternation with ring size, with the odd-membered rings being generally more stable than the even-membered rings. An alternation with ring size also occurs for enol contents of cyclanones and their 2-acyl derivatives[6] but, in that case, the even-membered rings are more enolic than the odd-membered rings.

Table I

Analyses of Copper Chelates of 2-Acetylcyclanones



Compd	n	Solvent,[a] mp (°C)	Calcd, % C	Calcd, % H	Found, %[b] C	Found, %[b] H
5	5	Et_2O-THF (238)	53.58	5.78	53.71	5.78
6	6	Et_2O (168-169)	56.20	6.49	56.31	6.74
7	7	THF (222.5-223.5)	58.44	7.08	58.14	7.06
8	8	THF (265 dec)	60.35	7.60	60.17	7.02
9	9	THF (199)	62.01	8.04	61.57	7.34
10	10	THF (184-187)	63.48	8.44	63.57	8.45
12	12	THF-$CHCl_3$ (208 dec)	65.91	9.09	65.75	9.11
15	15	THF (199 dec)	68.70	9.84	68.58	9.75

[a] Recrystallization solvent: Et_2O = ether; THF = tetrahydrofuran. [b] Analyses were performed by the Schwarzkopf Microanalytical Laboratory.

Table II

Some Infrared Absorption Peaks (Reciprocal Centimeters) of Chelates 5-15

Chelate	$\nu_{C=C}$	ν_{Cu-O}
5	1597	495
6	1573	452
7	1577	474
8	1569	452
9	1569	467
10	1564	460
12	1570	469
15	1574	471
Copper acetylacetone		455

As an alternative check on their relative stabilities,[7] the conductivities of the chelates were measured. It is reasoned that the more stable is the chelate, the smaller is the concentration of copper ion in solution and the smaller should be the conductivity. The data are given in Table III. The relative stabilities of the chelates, determined by the two methods, follow (in

Table III

Conductivity Data for Copper Chelates of 2-Acetylcyclanones in 75% Aqueous Pyridine

Chelate	M concn $\times 10^3$	Conductance, $L \times 10^5$ ohm^{-1} cm^{-1}	Vol. $V \times 10^{-4}$ ml	Equiv conductance, Λ ohm^{-1} cm^2 equiv^{-1}
5	4.93	1.948	10.136	1.974
6	4.64	8.004	10.077	8.618
7	4.83	6.199	10.340	6.412
8	4.61	7.628	10.840	8.267
9	4.64	9.168	10.780	9.883
10	5.10	9.853	9.803	9.659
12	4.99	8.828	11.248	11.248
15	4.66	7.151	10.739	7.679

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(7) Polarographic measurements with a dropping mercury electrode were also made on the chelates. Each chelate has two waves; however, the first wave blends in with the anodic curve from dissolution of Hg and the second wave [probably for Cu(I)] occurs at the same potential for all of the chelates. Since the potential for the first wave is not clearly discernable, the relative stabilities were not determinable by this method.

terms of ring size): from Cu–O frequencies $\mathbf{5} > \mathbf{7} > \mathbf{15} > \mathbf{12} > \mathbf{9} > \mathbf{10} > \mathbf{8} = \mathbf{6}$; from conductivities $\mathbf{5} \gg \mathbf{7} > \mathbf{15} > \mathbf{8} > \mathbf{6} > \mathbf{10} > \mathbf{9} > \mathbf{12}$. The two sequences are not identical but the odd-membered rings are generally more stable than the even-membered rings, excepting the C_9 ring.

Previous authors[8,9] have associated the ultraviolet absorption of metal chelates with the absorption by the ligand as perturbed by the metal ion. In some cases, there has been found a general correlation between $\Delta\lambda_m$ and the stability of the respective metal chelates, where $\Delta\lambda_m$ is the difference between λ_m of the chelate and chelating compound or enolate ion.[9-12] Consequently, it was hoped that the ultraviolet spectra would provide a measure of the relative stabilities of the chelates under study. Unfortunately, there are no significant differences in the λ_m values for these chelates in the ultraviolet region.

Absorption in the visible region by copper chelates is generally associated with d–d′ excitation, and it has been shown[13] that one can expect λ_m to shift to the red with decreasing stability of the metal chelates. Such a correlation could not be tested here because the absorption bands in the visible region for the chelates **5–15** were too broad for quantitative assignments of λ_m values. Neither could deviations from Beer's law be used as a criterion of degree of dissociation in solution, *i.e.*, relative stability, because all of the chelates obey Beer's law within the concentration range that can be used for the absorption measurements.

From this study, the Cu–O bond infrared frequencies of the copper chelates of 2-acetylcyclanones indicate that their relative stabilities alternate with ring size, with the odd-membered rings being generally more stable than the even-membered rings.[14] This alternating effect can be added to several other physical properties of alicycles found to oscillate with ring size, such as (1) the enol contents of cyclanones,[6] (2) $\lambda_m^{H_2O}$ in the ultraviolet region of the anions of nitrocyclanes,[15] (3) the nuclear magnetic resonance (nmr) chemical shifts for the vinyl protons in bromomethylenecyclanes,[16] (4) the half-wave potentials of bromocyclanes,[17] and (5) the carbonyl infrared frequencies of α-nitrocyclanones.[18]

Experimental Section

Preparation of Chelates.—The 2-acetyl derivatives of eight cyclanones were prepared by BF_3-catalyzed acetylations of the respective cyclanones following the method of Vogel.[19] The three smallest ketones were isolated: 2-acetylcyclopentanone, bp 65–68° (10^{-3} mm) [lit.[20] bp 72–75° (8 mm)]; 2-acetylcyclohexanone, bp 86–89° (5 mm) (lit.[21] bp 106–108° (14 mm)]; 2-acetylcycloheptanone, bp 96–99° (10^{-3} mm) [lit.[22] bp 107.5–110° (10 mm)]. The rest of the ketones were not isolated but converted directly into their copper chelates. All chelates were prepared by adding an excess of a saturated aqueous solution of copper acetate to an ether solution of a purified or crude ketone and the mixture was shaken for a few minutes. 2-Acetylcyclodecanone required the addition of a small volume of dilute ammonia to effect chelation. The precipitated chelates were filtered, washed with water, then with ether, dried in an oven at 90–100°, and recrystallized to constant melting point from tetrahydrofuran or ether. Their analyses are given in Table I.

Infrared Spectral Measurements.—Spectra for the chelates in the region 4000–200 cm^{-1} were obtained using Perkin-Elmer Models 21 and 421 spectrophotometers. Nujol mulls were found to be suitable down to 650 cm^{-1} using sodium chloride windows. The range where Nujol absorbs was examined by using hexafluorobutadiene solvent. Spectra below 700 cm^{-1} were measured on the 421 grating instrument (to ± 1 cm^{-1}) using Epolene C-3 film (Eastman Chemical Co.) and KBr windows. Essentially the same frequencies were obtained in the overlap region with Epolene C-3 and Nujol mulls but the intensity of the bands was much greater with the former.

Ultraviolet-Visible Spectral Measurements.—Ultraviolet-visible spectra of the chelates were measured with a Cary Model 14 recording spectrophotometer using matched quartz cells. The solutions were freshly prepared using tetrahydrofuran as a solvent in both regions.

Conductivity Measurements.—The conductivities were measured in 75% aqueous pyridine at 20° with a Wheatstone bridge assembly[23] and an oscilloscope for detecting zero current. The cell constant was determined using a standard KCl solution.

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Molecular Order in the Nematic Mesophases of 4,4′-Di-*n*-hexyloxyazoxybenzene and Its Mixtures with 4,4′-Dimethoxyazoxybenzene

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The ordered, anisotropic nature of a mesomorphic liquid (liquid crystal)[1,2] appears to have an orienting effect upon solute molecules dissolved in it. Linear, rod-shaped solute molecules have been shown to have a less disruptive effect on nematic mesophases than bulky, nonlinear molecules, presumably because the former adapt more readily to the parallel molecular arrangement in the liquid crystal, being oriented with their long axes parallel to those of the solvent molecules.[3]

Such behavior suggested that mesomorphic solvents might display selectivity toward solutes on the basis

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