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CYCLOPROPYL CONJUGATION WITH CHELATE RING OF β-DIKETONES

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Abstract—π-Conjugative effect of the cyclopropyl group on the chelate ring of β-diketone at the ground and excited states has been investigated by means of the spectroscopic methods. The spectral data of enolic β-diketones substituted with cyclopropyl group have been compared with those of the corresponding isopropyl substituted β-diketones. The chemical shift of —CH= proton of the chelate ring has been observed at lower magnetic field by the substitution with the cyclopropyl group. The changes in the chemical shift of the —OH proton are interpreted in terms of the preference of enolic structure in the asymmetrical β-diketones. The bathochromic shift of the $\pi \rightarrow \pi^*$ transition band of the enolic ring suggests that the more stabilization takes place at the excited state than at the ground state. The conjugative effect of the cyclopropyl group on the copper (II) chelate of β-diketones appears to be very small in comparison with that of enolized β-diketones.

THE π-conjugative interaction of a cyclopropyl group with an adjacent unsaturated bond has been an extremely interesting problem.[1] It has been of particular interest that the conformational preference of the cyclopropyl group reflects on the overlapping of *p*-orbital of an adjacent double bond.[2, 3] Even though many works on the cyclopropyl conjugation have been reported, a large number of them is concerned with the electronic spectra taking no account of the ground state.[4–7] The cyclopropyl conjugation at the ground state has recently been investigated by the PMR,[8–10] IR spectra,[11, 12] electron diffraction,[13, 14] and solvolysis.[15] Since the π-electron system of the enolic β-diketone associated with the intramolecular H-bond is sensitively perturbed by the substituent, we have attempted to study the conjugative effect of the cyclopropyl group on the chelate ring at the ground and the excited states.

β-Diketones were prepared from the corresponding ketone and ester using sodium amide.[16] As has been pointed out by Hammond *et al.*,[17] a bulky substituent at the 1 or 3 position increases the enol content owing to repulsive interaction between 1- and 3-substituents. The NMR and IR spectra of the cyclopropyl substituted β-diketones exhibit similar high enolization as observed for the isopropyl substituted β-diketones. Proton chemical shifts of the enol form are summarized in Table 1. All of them showed more than 90% of the enol tautomer in carbon tetrachloride estimated from the ratio of integration of the $-CH_2-$ protons of the keto form and the —CH= proton of the enol form. As an example, the NMR spectrum of 1,3-dicyclopropyl-1,3-propanedione (III) is given in Fig 1.

Two characteristic chemical shifts of the —CH= and O—H···O protons of the chelate ring can be used to evaluate the changes in the π-conjugative system and the strength of intramolecular H-bond. The chemical shifts of the —CH= of the cyclopropyl substituted β-diketones slightly resonate at lower magnetic field relative to those of the corresponding isopropyl substituted β-diketones. A similar trend has been

TABLE 1. NMR SPECTRA OF THE ENOLIC β-DIKETONES* (τ in ppm)

	R_1	R_2	$\tau_{-CH=}$	τ_{OH}	R_1	R_2
I	$CH(CH_3)_2$	$CH(CH_3)_2$	4·56	−5·34		7·56 (2H, m),** 8·84 (8H, d)**
II	C_3H_5	$CH(CH_3)_2$	4·49	−5·66	8·40 (1H, m), 9·10 (4H, m)	7·62 (1H, m), 8·85 (6H, d)
III	C_3H_5	C_3H_5	4·35	−5·76		8·45 (1H, m), 9·02 (8H, m)
IV	$CH(CH_3)_2$	C_6H_5	3·93	−6·32	7·44 (1H, m), 8·80 (6H, d)	2·20 (2H, m), 2·60 (3H, m)
V	C_3H_5	C_6H_5	3·84	−6·27	8·16 (1H, m), 8·94 (4H, m)	2·25 (2H, m), 2·65 (3H, m)
VI	$CH(CH_3)_2$	$2\text{-}C_4H_3O$	4·00	−5·37	8·80 (6H, d), 7·47 (1H, m)	3·50 (1H, m), 2·94 (1H, d) 2·53 (1H, d)
VII	C_3H_5	$2\text{-}C_4H_3O$	3·93	−5·29	8·29 (1H, m), 8·90 (4H, m)	3·50 (1H, m), 3·03 (1H, d) 2·54 (1H, d)
VIII	$CH(CH_3)_2$	$2\text{-}C_4H_3S$	4·10	−5·77	7·50 (1H, m), 8·80 (6H, d)	2·95 (1H, m), 2·42 (1H, d) 2·53 (1H, d)
IX	C_3H_5	$2\text{-}C_4H_3S$	3·96	−6·00	8·34 (1H, m), 8·92 (4H, m)	2·98 (1H, m), 2·40 (1H, d) 2·55 (1H, d)
X	$CH(CH_3)_2$	CF_3	4·12	−3·53	7·45 (1H, m), 8·78 (6H, d)	
XI	C_3H_5	CF_3	3·98	−4·69	8·22 (1H, m), 8·80 (4H, m)	

* Measured in 3% CCl_4 solns using TMS as an internal standard.
** d and m denote doublet and multiplet, respectively.

observed in cyclopropyl substituted olefinic esters, of which α—CH= proton is slightly deshielded by 0·03–0·15 ppm.[18] The chemical shift of the enolic proton provides proper measure of the strength of an intramolecular H-bond.[19] The replacement of isopropyl group with cyclopropyl group causes a downfield shift of the enolic proton (case I: II with III, VIII with IX, and X with XI). On the other hand, comparisons of IV with V and VI with VII reveal the slight shielding-effect (case II). The shifts of the C=O stretching due to cyclopropyl substitution indicate somewhat similar tendency to the NMR spectra as shown in Table 2. The C=O stretching shifts

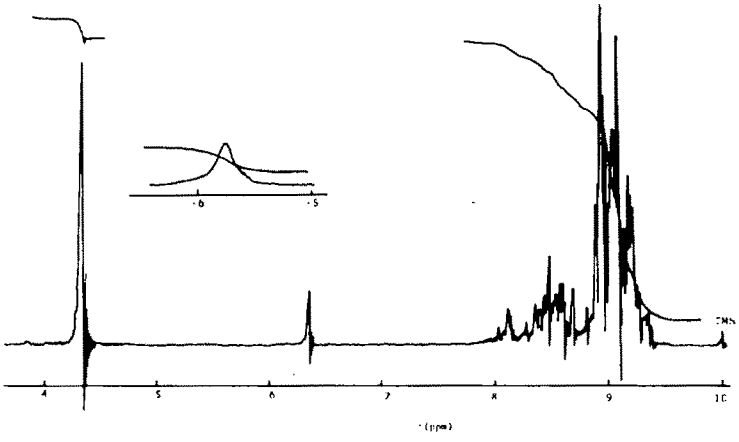
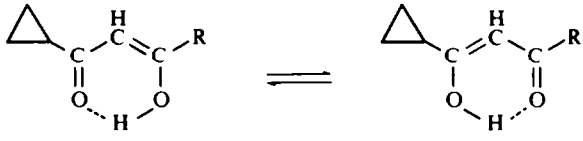


Fig 1. The NMR Spectrum of 1,3-Dicyclopropyl-1,3-propanedione

TABLE 2. UV SPECTRA AND THE C=O STRETCHING OF THE ENOLIC β-DIKETONES

Compound	λ^{max} (mμ)	log ε	ν(C=O)(cm^{-1})
I	273·5	4·13	1613
II	277·0	4·12	1610
III	284·0	4·11	1584
IV	307·0	4·42	1573
V	315·0	4·23	1571
VI	310·0	4·36	1610
VII	323·5	4·43	1607
VIII	318·0	4·26	1605
IX	331·0	4·25	1582
X	282·5	3·84	1612
XI	295·5	3·85	1598

to lower frequency region are also appreciable (14–26 cm^{-1}) for case I, being only few wave numbers for case II. Strictly speaking, an argument with the C=O stretching seems to be qualitative in our system, because of superposition of the C=C stretching.[20]



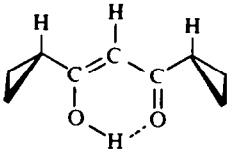
A B

There exist possible interconvertible enol isomers (A) and (B) in asymmetric β-diketones, even though the potential barrier between two isomers appears to be very small. It is, however, difficult to determine whether (A) or (B) is predominant structure at the equilibrium from the NMR spectra. Averaged chemical shifts of (A) and (B) are observable owing to a rapid interconversion.[21] If one enol structure exceeds the other, it is expected that the averaged values are indicative of the chemical shifts belonged to the former. According to this consideration, it is possible to explain that the replacement of isopropyl group with cyclopropyl group increases or decreases the strength of the H-bond. An electron-supplying ability of the cyclopropyl group adjacent to the CO group enhances the electron density on the CO oxygen through the resonance and inductive effects, which results in increasing the strength of the hydrogen bond in (A) form. To the contrary, the cyclopropyl group in (B) form increases the electron densities of the enol oxygen (due to its inductive effect) and CO oxygen (mainly due to its resonance effect). This might result in the formation of weaker H-bond.

The absorption of the $\pi \rightarrow \pi^*$ bands of β-diketones are summarized in Table 2. Replacement of isopropyl group with cyclopropyl group causes bathochromic shifts from 3·5 to 13 mμ. Among them, β-diketones containing furyl (VII), thienyl (IX), and trifluoromethyl (XI) groups exhibit larger shifts than those of II and IV. The cyclopropyl group seems to contribute to an effective stabilization due to the charge separation in the excited state through conjugation.

A bathochromic shift may be attributed to the electronic effect of the R-group on charge transfer excitation as observed in cyclopropyl olefins[5] and β-cyclopropyl-α,β-unsaturated CO systems.[18] Since a change in electronic spectra is related to the energy difference between the ground state and the excited state, the cyclopropyl group seems to show stronger interaction with π-electron system of the enolic ring in the excited state than in the ground state.

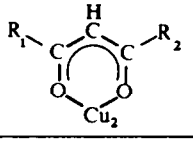
Conformational study on cyclopropyl methyl ketone by the electron diffraction[14] has suggested that s-*cis* rotational isomer is preferential rather than s-*trans* conformer at the ground state. Furthermore, it has been proposed that the s-*trans* rotational isomer is lower energy conformer on the basis of analysis of NMR spectra of vinyl-cyclopropane. These results lead us to suppose that one of two cyclopropyl rings of 1,3-dicyclopropyl-1,3-propanedione (III) is placed in s-*cis* conformation to the carbonyl and the other one is s-*trans* to perform maximum overlap with 2*p*-orbitals of the enolic ring.[22]



III

In IR spectra of II in the liquid phase, intensities of three bands at 2950, 889, and 401 cm^{-1} were extremely decreased in comparison with the spectrum in the solid state at 110°K. The ratio of the intensities of the C=O stretching due to the keto and enol forms did not change so much in both liquid and solid phases. Therefore, this fact seems to give an evidence of presence of conformational isomers in the liquid phase, the quantitative discussion on the conformational behaviour in our system being difficult at the present time.

TABLE 3. UV SPECTRA OF COPPER (II) CHELATES OF 1,3-DIKETONES*



R_1	R_2	λ_{max} (mμ),	(log ε)
$CH(CH_3)_2$	$CH(CH_3)_2$	251·1 (4·08)	299·9 (4·36)
C_3H_5	$CH(CH_3)_2$	249·1 (4·29)	298·5 (4·49)
C_3H_5	C_3H_5	248·2 (4·36)	300·0 (4·59)
$CH(CH_3)_2$	C_6H_5	261·0 (4·45)	325·4 (4·57)
C_3H_5	C_6H_5	258·5 (4·37)	327·4 (4·55)
$CH(CH_3)_2$	2-C_4H_3O		336·2 (4·59)
C_3H_5	2-C_4H_3O		336·5 (4·76)
$CH(CH_3)$	2-C_4H_3S	266·5 (4·29)	340·5 (4·57)
C_3H_5	2-C_4H_3S	265·8 (4·22)	341·0 (4·54)

* measured in methylene chloride.

Cyclopropyl conjugation with the metal chelate (quasi-aromatic system) is of interest in comparison with phenylcyclopropane.[4, 8] However, a substitution with cyclopropyl group has now shown such significant changes in both ground and excited states as is seen in the enolic ring. Table 3 lists UV spectra of the copper (II) chelates of β-diketones. The absorption maxima at around 250 mμ assigned to σ(ligand) → d_{x^2}(metal) transition[23] reveal very small shifts to lower wave length, and the bands of 290–340 mμ due to the π → π* transition[24] of the metal chelate do not show appreciable differences by the replacement of the isopropyl group with the cyclopropyl. The chelated C⋯O stretching vibrations appeared at 1580 cm^{-1} were also insensitive to the substitution with cyclopropyl group. Therefore, it seems to suggest that the conjugative effect of the cyclopropyl group on the copper (II) chelate is negligible in the ground state as well as in the excited state.

EXPERIMENTAL

Preparation of 1-*cyclopropyl*-4-*methyl*-1,3-*pentanedione* (II). A soln of 8·04 g (0·096 mole) cyclopropylmethylketone in 100 ml anhyd ether was slowly added to a suspension of 7·0 g (0·18 mole) finely pulverized $NaNH_2$ under vigorous stirring for 30 min. To the reaction mixture was added dropwise 32·0 g (0·27 mole) ethyl isobutyrate followed by further reaction at room temp for 3 hr. The gelatinous mixture was poured into ice-water and neutralized by 6N HCl. The β-diketone was separated by treatment of aqueous copper(II) acetate in the form of bis-(1-cyclopropyl-4-methyl-1,3-pentanediono)-copper(II). The copper(II) chelate recrystallized from chloroform–n-hexane (1 : 5) was hydrolysed by 6N HCl. The β-biketone was recovered by extraction with ethyl ether. The ether extract was washed with water and dried over Na_2SO_4. Distillation at reduced press afforded 6·5 g colourless liquid, b.p. 54·0–55·5°/6 mm, 44% yield based on ketone. (Found: C, 9·43; H, 70·32. Mol. wt. by mass spectrum 154. $C_9H_{14}O_2$ requires: C, 9·15; H, 70·12, Mol. wt. 154).

1,3-*Dicyclopropyl*-1,3-*propanedione* (III) was obtained in a yield of 49·4% (7·5 g) using 6·7 g cyclopropyl methyl ketone and 11·4 g ethyl cyclopropanecarboxylate, b.p. 86–88°/8 mm. (Found: C, 8·15; H, 71·75. Mol. wt. by mass spectrum 152. $C_9H_{12}O_2$ requires: C, 7·95; H, 71·02, Mol. wt. 152).

1-*Cyclopropyl*-3-(2-*furyl*)-1,3-*propanedione* (VII) was obtained in a yield of 32·0% (3·3 g) using 12·5 g α-furancarboxylic acid methyl ester and 4·2 g cyclopropyl methyl ketone, b.p. 91–92°/6 mm. (Found: C, 5·96; H, 67·98. Mol. wt. by mass spectrum 178. $C_{10}H_{10}O_3$ requires: C, 5·91; H, 67·98% Mol. wt. 178).

1-*Cyclopropyl*-3-(2-*thienyl*)-1,3-*propanedione* (IX) was obtained in a yield of 52·0% (9·3 g) using 15·0 g 2-acetyl thiophene and 18·0 g ethyl cyclopropanecarboxylate, b.p. 142–144°/4 mm. (Found: C, 5·20; H, 62·42; S, 16·52. Mol. wt. by mass spectrum 194. $C_{10}H_{10}O_2S$ requires: C, 5·12; H, 61·85; S, 16·49, Mol. wt. 194).

1,1,1-*Trifluoro*-4-*cyclopropyl*-2,4-*butanedione* (XI) was prepared from 25·0 g ethyl trifluoroacetate and 8·0 g cyclopropyl methyl ketone. The ether extract was refluxed with P_2O_5 for 5 hr. Distillation gave 5·3 g (31% yield) of colourless liquid, b.p. 129–132°. (Found: F, 30·85. $C_7H_7O_2F_3$ requires: F, 31·65%). Mass spectrum showed M^+ at 180 (base peak) and the prominent peaks at 139, 111, 69, 41 and 39. The copper chelates were prepared from β-diketone and aqueous copper(II) acetate and purified by recrystallization from chloroform–n-hexane. (Table 4.)

TABLE 4. THE COPPER (II) CHELATES OF 1-CYCLOPROPYL-1,3-DIKETONES

	mp (°C)	Formula	Calcd (%) C	Calcd (%) H	Found (%) C	Found (%) H
Bis-1,3-dicyclopropyl-1,3-propanediono)-Cu(II)	156–158	$C_{18}H_{22}O_4Cu$	6·06	59·08	6·10	58·86
Bis-(1-cyclopropyl-4-methyl-1,3-pentanediono)-Cu(II)	102–104	$C_{18}H_{26}O_4Cu$	7·09	58·43	6·95	58·13
Bis-(1-cyclopropyl-3-thienyl-1,3-propanediono)-Cu(II)	212–214	$C_{20}H_{18}O_6Cu$	4·35	57·48	4·48	57·43
Bis-(1-cyclopropyl-3-furyl-1,3-propanediono)-Cu(II)	260–262	$C_{20}H_{18}O_4Cu$	4·06	53·33	4·11	53·33

Spectral measurements. NMR spectra were determined at 60 Mc/S with a JNM-C-60 spectrometer. IR spectra were measured in CCl_4, using Jasco IR spectrophotometer Model 402 G. Measurement of UV spectra were carried out in n-hexane for the β-diketones and in methylenedichloride for the copper(II) chelates using HITACHI spectrophotometer model EPS-3T. Mass spectra were obtained with a HITACHI Model RMS-4 Mass spectrometer.

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