MAGNITUDE OF THE HOMOCONJUGATION EFFECT IN CHIRAL TWO-RING ENAMINO KETONES

V. M. Potapov, G. V. Grishina, and G. N. Koval'

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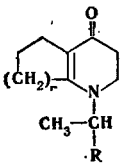
On the basis of circular dichroism (CD) and optical rotatory dispersion (ORD) data and an examination of the preferred conformations of two-ring enamino ketones Ia-c [1] with an α-phenylethyl substituent attached to the nitrogen atom, we have proposed the existence of a homoconjugation effect [2] of the enamino ketone and phenyl chromophore groups as a result of the drawing together in space of their π orbitals. An even greater increase in the molecular ellipticity of the positive band of the $\pi-\pi^*$ transition of the enamino ketone chromophore, which attests to intensification of homoconjugation, was observed in the CD spectra of enamino ketones IIa-c, the chromophores in which are separated by three σ bonds.



I-III a-c

I a n=1, R=C_6H_5, b n=2, R=C_6H_5, c n=3, R=C_6H_5; II a n=1, R=$CH_2C_6H_5$, b n=2, R=$CH_2C_6H_5$, c n=3, R=$CH_2C_6H_5$; III a n=1, R=C_2H_5, b n=2, R=C_2H_5, c n=3, R=C_2H_5

An examination of the ORD data (in heptane) for model enamino ketones IIIa-c, in which only an enamino ketone chromophore (R = C_2H_5) is present, also showed the presence of a positive Cotton effect with a peak at 350-355 nm and a valley at 315-317 nm with molecular amplitudes +78 (IIIa), +50 (IIIb), and +13.8 (IIIc). These values are substantially lower than the corresponding molecular amplitudes of the Cotton effects for enamino ketones I and II [+480 (Ia), +297 (Ib), +211 (Ic), +652 (IIa), and +454 (IIc)]. The difference between the magnitudes of the molecular amplitudes of the Cotton effects of enamino ketones I, II, and III consequently characterizes the magnitude of the homoconjugation effect of the enamino ketone and phenyl chromophore groups in I and II.

LITERATURE CITED

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