Dissymmetrically Perturbed Aromatic Chromophore in Stereoregular Copolymers of (*R*)-3,7-Dimethyl-1-octene with Styrene

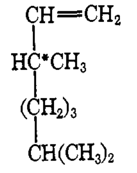
Sir:

Optically active alkylaryl hydrocarbons show, in the 260-mμ region, a very small Cotton effect[1,2] connected with a $\pi \rightarrow \pi^*$ transition of the aromatic chromophore.

Continuing our research[3] on conformational rigidity[4,5] and optical activity in acyclic low and high molecular weight hydrocarbons, we have studied copolymers of (*R*)-3,7-dimethyl-1-octene (I) with styrene (II) to investigate the possible influence of conformational rigidity on the rotational strength of the formally forbidden $\pi \rightarrow \pi^*$ transition of the aromatic chromophore.

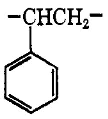
Styrene (II) is known[6,7] to copolymerize with branched α olefins in the presence of various Ziegler–Natta catalysts to give crystalline copolymers containing isotactic stereoblocks deriving from both comonomers.[8]

In an attempt to prepare isotactic macromolecules containing isolated units, III, in blocks of units (IV) derived from (*R*)-3,7-dimethyl-1-octene (I), we have copolymerized at room temperature II with I (optical purity 95%) in the presence of the $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ (molar ratio 1:3) catalytic system using a molar ratio I:II = 10.

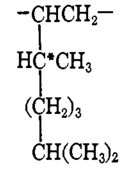


$CH_2{=}CH{-}C^*H(CH_3){-}(CH_2)_3{-}CH(CH_3)_2$

I



III



$-CH(C^*H(CH_3)(CH_2)_3CH(CH_3)_2)CH_2-$

IV

The purified copolymer was fractionated by boiling solvent extraction using acetone, diethyl ether, and cyclohexane in that order. The polymer was completely soluble in cyclohexane, showing the absence of isotactic polystyrene. The concentration of unit III in each fraction was determined (Table I) by measuring the ultraviolet absorption of dilute solutions of the polymer in chloroform[8,9] using the band at 262 mμ.[10]

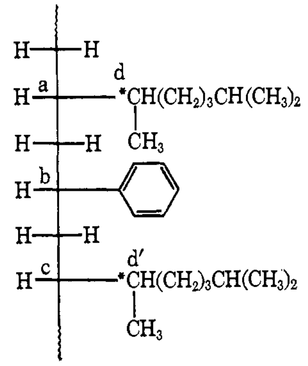
Table I. Fractionation by Solvent Extraction of (*R*)-3,7-Dimethyl-1-octene[a]–Styrene (I–II) Copolymer and of Poly[(*R*)-3,7-dimethyl-1-octene][a]

	I–II copolymer			Poly[(*R*)-3,7-dimethyl-1-octene]	
Fraction extracted with boiling	%[b]	$[\alpha]^{25}D$,[c] deg	Units deriving[d] from II, mol %	%[b]	$[\alpha]^{25}D$,[e] deg
Acetone	6.7	ND[f]	ND[f]	2.3	−32.5
Diethyl ether	34.0	−83	20.4	4.7	−59.5
Cyclohexane	59.3	−87	4.4	93.0	−92

[a] Optical purity of (*R*)-3,7-dimethyl-1-octene ~95%. [b] On the total weight of methanol-insoluble polymer. [c] In $CHCl_3$ solution. [d] Calculated from the intensity of the absorption band at 262 mμ, assuming ϵ_{262} 0 for poly[(*R*)-3,7-dimethyl-1-octene]. [e] In hydrocarbon solution. [f] Not determined.

As reported in Table I, the diethyl ether extractable fraction is much larger in the case of the copolymer (34.0%) than in the case of the homopolymer of I (4.7%). This fraction, which contains 20.4 mol % of units III, has $[\alpha]^{25}D$ very close to that of the cyclohexane-extractable fraction in which only 4.4 mol % of units III are present. Both fractions are crystalline, the crystallinity being of the type shown by poly[(*R*)-3,7-dimethyl-1-octene]. Both fractions, in $CHCl_3$ solution, have very similar circular dichroism spectra (Roussell-Jouan dichrograph II) which show (Figure 1, curve A), in agreement with the uv absorption spectra, a band with fine structure between 275 and 245 mμ.[11] $\Delta\epsilon_{max}$, based on one unit III,[12] at 262 mμ is −0.27 for the diethyl ether extractable and −0.24 for the cyclohexane extractable fraction. In the copolymer macromolecules, at least for what concerns groups V[13] (represented as Fischer projection for the main chain), that is, one unit III derived from styrene isolated between two units IV, taken as part of a stereoregular section of isotactic type, the two asymmetric carbon atoms d and d′ of the lateral chains are in the δ position with respect to the phenyl group and both have *R* absolute configuration.

As shown in the Fischer projection V the tertiary carbon atoms of the main chain of the two IV units,



V

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(1) L. Verbit, *J. Am. Chem. Soc.*, **87**, 1617 (1965).

(2) A. Moscowitz, A. Rosenberg, and A. E. Hansen, *ibid.*, **87**, 1813 (1965).

(3) P. Pino, *Advan. Polymer Sci.*, **4**, 393 (1965), and references cited therein.

(4) A. Abe and M. Goodman, *J. Polymer Sci.*, *A*, **1**, 2193 (1963).

(5) H. Morawetz, "Macromolecules in Solution," Interscience Publishers, New York, N. Y., 1965, p 241.

(6) I. H. Anderson, G. M. Burnett, and P. J. T. Tait, *Proc. Chem. Soc.*, 225 (1960).

(7) C. G. Overberger, and K. Miyamichi, *J. Polymer Sci.*, *A*, **1**, 2021 (1963).

(8) I. H. Anderson, G. M. Burnett, and W. C. Geddes, *Europ. Polymer J.*, **3**, 161 (1967).

(9) G. Loux and G. Weill, *J. Chim. Phys.*, **61**, 484 (1964).

(10) As ϵ_{262} of the copolymer could, in principle, differ from ϵ_{262} of isotactic polystyrene, the results have been controlled by infrared spectroscopic analysis using the band at 762 cm^{-1}. For a copolymer sample 17.9% of unit III was found by uv analysis and 17.0% by ir analysis. We thank Dr. E. Benedetti for performing the ir analysis.

(11) P. Crabbé and W. Klyne, *Tetrahedron*, **23**, 3449 (1967); L. Verbit, *J. Am. Chem. Soc.*, **88**, 5340 (1966).

(12) $\Delta\epsilon = d \times 10^{-5}/(cl)$, where d = recorded deflection in millimeters, l = spectral light path of the cell in centimeters, and c = moles/liter for VI and (grams of copolymer times weight per cent of unit III)/(molecular weight of unit III times liter) for the copolymer.

(13) The group V is the most probable taking in account the catalytic system used and the low concentration of styrene units. V cannot be properly called isotactic despite all the lateral groups being on the same side of the main chain, as in isotactic macromolecules from vinyl monomers [G. Natta, P. Pino, and G. Mazzanti, *Gazz. Chim. Ital.*, **87**, 528 (1957)]. In fact, the tertiary carbon atoms of the main chain, a, b, and c, have not the same absolute configuration, contrary to what generally happens for short sections of isotactic vinyl polymers. According to Cahn, Ingold, and Prelog nomenclature [R. S. Cahn, C. I. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956)], in fact a has *S* absolute configuration, b is pseudoasymmetric with *s* configuration, and c has *R* absolute configuration, even supposing V was included in a chain of units IV having infinite length.

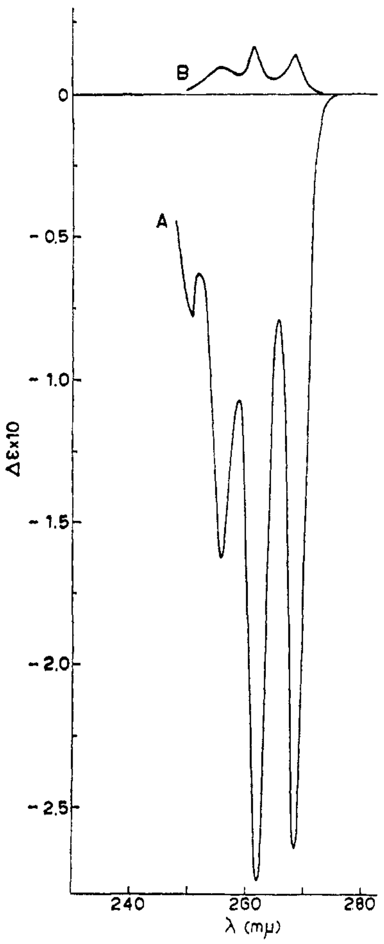
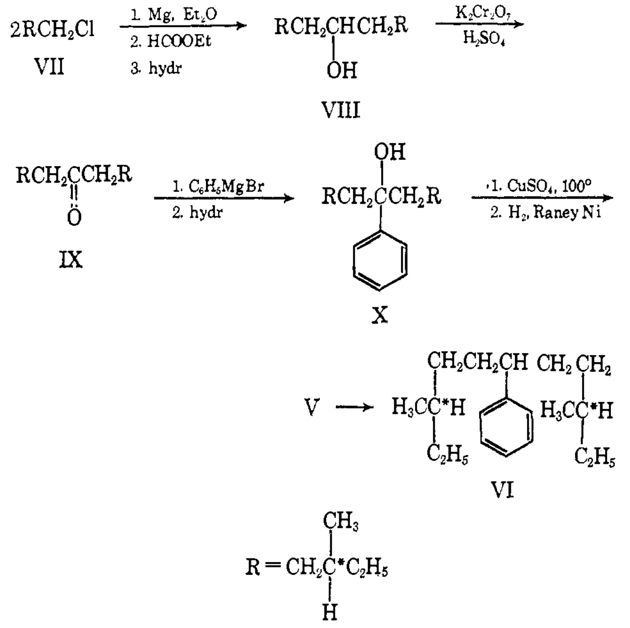


Figure 1. Circular dichroism in chloroform solution at 25° of (3*S*,9*S*)-3,9-dimethyl-6-phenylundecane (B) and of the diethyl ether extractable fraction (Table I) of the styrene–(*R*)-3,7-dimethyl-1-octene copolymer (A); Δε is based on one unit of III deriving from styrene.[12]

which are in the γ position with respect to the phenyl group, have opposite absolute configurations, and the sum of their possible contributions to optical rotation should be vanishing small.

As a low molecular weight model of V we have therefore taken (3*S*,9*S*)-3,9-dimethyl-6-phenylundecane (VI) in which the two asymmetric carbon atoms have the same absolute configuration and are in the δ position with respect to the phenyl group. For the preparation of VI a scheme based on (*S*)-1-chloro-3-methylpentane (VII) was used. VII, $[\alpha]^{25}\mathrm{D}$ +19.0° (neat) and optical purity ~95%,[14] was converted to the Grignard derivative, 2 moles of which, with ethyl formate, gave (3*S*,9*S*)-3,9-dimethylundecan-6-ol (VIII): bp 142–143° (20 mm); $n^{25}\mathrm{D}$ 1.4408; $[\alpha]^{25}\mathrm{D}$ +16.2° (*c* 7.934, MeOH). *Anal.* Calcd for $C_{13}H_{28}O$: C, 77.92; H, 14.08. Found: C, 77.87; H, 14.13. VIII was oxidized to the corresponding (3*S*,9*S*)-3,9-dimethylundecan-6-one (IX): bp 131–132° (20 mm); $n^{25}\mathrm{D}$ 1.4348; $[\alpha]^{25}\mathrm{D}$ +16.8° (*c* 5.062, MeOH). *Anal.* Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.54; H, 12.92. IX with C_6H_5MgBr gave (3*S*,9*S*)-3,9-dimethyl-6-phenylundecan-6-ol (X): bp 149–150° (2 mm); $n^{25}\mathrm{D}$ 1.4922; $[\alpha]^{25}\mathrm{D}$ +15.3° (*c* 3.650, MeOH). *Anal.* Calcd for $C_{19}H_{32}O$: C, 82.54; H, 11.66. Found: C, 82.75; H, 11.79. X was dehydrated with $CuSO_4$ at 100° to a mixture of two olefins which was hydrogenated at 70° in the presence of Raney Ni to VI: bp 102–104° (0.2–0.3 mm); $n^{25}\mathrm{D}$ 1.4803; $[\alpha]^{25}\mathrm{D}$ +14.2° (*c* 0.464, $CHCl_3$). *Anal.* Calcd for $C_{19}H_{32}$: C, 87.61; H, 12.39. Found: C, 87.56; H, 12.26. VI shows in $CHCl_3$ a CD band with fine structure in the same wavelength region of the copolymers (Figure 1, curve B), but with much lower intensity, $\Delta\epsilon_{\max}$ at 262 mμ being +0.017.[12]



Considering the mild conditions used in all the steps reported in the scheme and that the reactions involved take place on atoms in β or γ position with respect to the asymmetric carbon atoms, it is reasonable to assume that the prepared sample of VI has an optical purity not markedly lower than that of VII.

This assumption is confirmed by the comparison of the ORD (Cary Model 60) of VI and of (*S*)-2-phenylbutane (XI), having $[\alpha]^{25}\mathrm{D}$ +28.4° (neat) and hence[15] optical purity of about 98%. In both cases a Cotton effect centered at 260 mμ is present with amplitude[16] of about 0.6 for VI and 0.8 for XI. The copolymer shows also a Cotton effect at the same wavelength, but the amplitude, based on one unit III, is much larger (9.0).

The fact that the copolymers and (3*S*,9*S*)-3,9-dimethyl-6-phenylundecane show very similar uv absorption spectra and Cotton effect at the same wavelength, differing only in the amplitude, seems to indicate the absence of significant electronic interactions among phenyl groups[17] contained in the same macromolecule of copolymer.

The data however do not exclude the presence of short blocks of units III, as isotactic and atactic polystyrene show very similar uv absorption spectra.[9]

The higher rotational strength of the $\pi \rightarrow \pi^*$ aromatic transition at about 260 mμ in the copolymers with respect to the low molecular weight models is attribut-

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[14] L. Lardicci and P. Pino, *Gazz. Chim. Ital.*, **91**, 441 (1961).

[15] L. Lardicci, private communication. The data are in good agreement with that reported by Verbit.[1]

[16] P. Crabbé, "Optical Rotatory Dispersion and Circular Dicroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965, p 17.

[17] D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954).

able to the conformational rigidity of the units III derived from styrene, inserted into the copolymer macromolecules.

The above conformational rigidity should derive from the fact that unit III is incorporated into isotactic blocks of units IV which have been reported to have a helical conformation with one prevailing screw sense.[18]

The reported results indicate that the insertion of units III derived from styrene into the chains of optically active poly-α-olefins can function as an electronic probe[19] for exploring macromolecular conformation in the vicinity of the chromophore.

[18] P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Montagnoli, *Makromol. Chem.*, **61**, 207 (1963).

[19] The incorporation of aromatic compounds in polymers to investigate macromolecular conformations is known in protein chemistry (H. Morawetz, "Macromolecules in Solution," Interscience Publishers, New York, N. Y., 1965, pp 219–221, and references cited therein).

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Received May 18, 1968

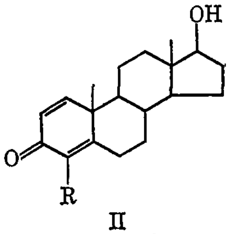
Efficiencies of Quenching of Short-Lived Excited Triplet States of Ketones with Dienes[1,2]

Sir:

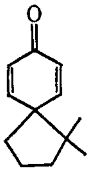
Recently, two of us reported that the reactive triplet excited state of α-santonin (I) was quenched much more efficiently by 1,3-cyclohexadiene than by piperylene.[3] We have now found that this effect is general for a series of 2,5-cyclohexadienones and also with a bicyclo[3.2.0]hept-6-en-2-one (V). The results are given in Table I as slopes of linear Stern–Volmer quenching plots using 1,3-cyclohexadiene ($k_q\tau_0$) and *trans*-piperylene ($k'_q\tau_0$) as triplet quenchers. Triplet energies of the ketones are given where known from phosphorescence emission, or determined with a graded series of sensitizers and quenchers. Also included are some quenching results for dimerization of cyclopentenone.[4]

With α-santonin, it was shown that, at the high concentration limit, quenching with 1,3-cyclohexadiene was due only (95–98%) to triplet-energy transfer,[3] according to the quantum yield of cyclohexadiene dimers.[5] These dimers[5] were noted in all runs using cyclohexadiene. Where adducts of quencher and ketone were indicated from glpc analysis by a reaction concomitant with energy transfer, the former process was always of much less importance.

It is generally assumed that triplet-energy transfer in solution occurs at a diffusion-controlled rate as long as the triplet energy of the donor is greater than that of the acceptor by at least 3 kcal/mol.[6] Accordingly, energy transfer to 1,3-cyclohexadiene (E_T = 54 kcal)[7,8] and *trans*-piperylene (E_T = 59–60 kcal)[8] ought to be equally efficient for most, if not all, of the ketones in Table I.[9] It is particularly remarkable that the relative efficiencies of energy transfer to the two dienes, given as k_q/k'_q, increase as the absolute efficiencies given by the Stern–Volmer slopes decrease. It is clearly not warranted to make the assumption that energy transfer to either diene is occurring at the diffusion-controlled rate.[10] All piperylene plots are linear up to very high concentrations of diene, but upward curvature[10] is beyond experimental error on cyclohexadiene quenching (>4 *M*) of α-santonin and II, R = Me. It is not possible to extract from the data values of either k_q or τ_0 and hence of any rate constants for specific processes. It is likely that the triplet lifetime, τ_0, is increasing, although perhaps not monotonously, as one proceeds down the table.



II



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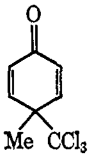

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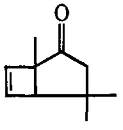

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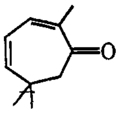

VI

Differential quenching cannot be solely an effect of short triplet lifetimes, since the effect is not observed (within an experimental error of about 10%) with cyclopentenone whose lifetime is similar to those of other ketones in Table I.[4,11–13] Whether or not photodimerization occurs from T_1 or T_2, τ_0 is a function of cyclopentenone concentration, which was varied by a factor of 50 without observation of significant differential quenching.[13]

The results can be understood in the model framework for triplet-energy transfer proposed by Wagner.[10] Using his terminology[10] we assume that $k_{dif} = k'_{dif}$ and that $k_{-dif} = k'_{-dif}$,[14] but that $k_{et} \neq k'_{et}$, where k refers

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[1] Part XVIII of a series on the photochemistry of unsaturated ketones in solution. Part XVII: D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, in press.

[2] Research supported by grants from the U. S. Army Research Office, Durham (Project 4019-C), and the National Science Foundation (GP 7433).

[3] D. I. Schuster and A. C. Fabian, *Tetrahedron Letters*, 1301 (1968).

[4] P. E. Eaton and W. S. Hurt, *J. Am. Chem. Soc.*, 88, 5038 (1966).

[5] D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **86**, 5202 (1964).

[6] (a) For an extensive review of triplet energy transfer, see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968). (b) See also N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 116 ff, and J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., 1966, p 348 ff, and references cited therein.

[7] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[8] G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964); R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

[9] It is recognized that emission spectroscopy alone may not give accurate values for E_T, and that relaxed lower energy nonemitting triplets may be involved,[6a] although there is no evidence at present in support of this suggestion. However, with the low-energy triplets of eucarvone (E_T = 60 ± 1 kcal) and cyclopentenone (E_T = 61 kcal), differential quenching is *not* observed.

[10] P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5715 (1967); P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968).

[11] P. de Mayo, J. P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967).

[12] J. L. Ruhlen and P. A. Leermakers, *ibid.*, **89**, 4944 (1967).

[13] Assuming that k_q in benzene = 5×10^9 l. mol^{-1} sec^{-1} in this case,[10] τ_0 at 6.1 *M* ketone is 4.7×10^{-10} sec. From our studies and data of Eaton[4] (Φ = 0.27 at 3.0 *M* ketone), k_d/k_r = 1.08 and $k_r = 3 \times 10^8$ l. mol^{-1} sec^{-1}.

[14] This second assumption is probably not strictly correct, although it is only necessary for our purposes that the rate constants for diffusion of the quencher away from the triplet do not differ greatly.