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REVISED STRUCTURE OF DIASTEREOMERIC 3,8-DI-*t*-BUTYLSPIRO[4.4]NONANE-1,6-DIONES

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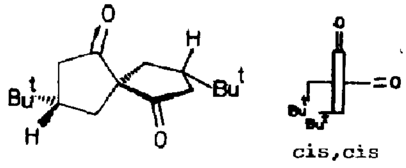
Abstract: The recently assigned diastereomeric configuration of 3,8-di-*t*-butylspiro[4.4]nonane-1,6-dione has been revised based on the X-ray analysis.

Recently, we have reported the syntheses of three optically active diastereomers of 3,8-di-*t*-butylspiro[4.4]nonane-1,6-dione (**Ia**, **Ib**, and **Ic**) and the tentative assignment of their relative configurations of chiral centers based on the analysis of the NMR spectra, giving *trans,trans*-, *cis,trans*-, and *cis cis*-configuration to **Ia**, **Ib**, and **Ic**, respectively.[1]

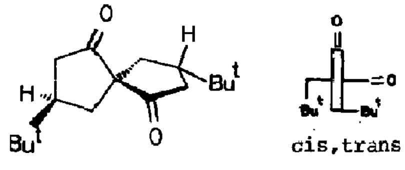
However, recent X-ray analysis of the derivative of **Ia**[2] has clearly revealed the *cis,cis*-configuration for **Ia**.

Therefore, we report here the revised structures of **Ia** and **Ic** as *cis,cis* (*3S,5R,8S*) and *trans,trans* (*3R,5R,8S*), respectively, and the examination of c.d. spectra based on the finally assigned structures.

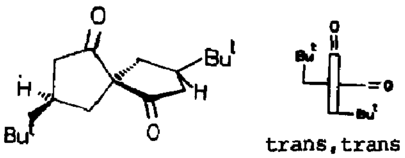
The c.d. spectra of (*3S,5R,8S*)-(−)-**Ia**, (*3R,5R,8S*)-(+)-**Ib**, (*3R,5R,8R*)-(+)-**Ic**, and the parent compound, (*5R*)-(+)-spiro[4.4]-nonane-1,6-dione (**II**) are shown in Figure 1. The C_2-symmetrical structure of **II** has already been determined by X-ray analysis and Valence-Force calculation, and its octant projection given as shown in Figure 2.[3]



Ia $[\alpha]_{589}$ −51.7° (MeOH)



Ib $[\alpha]_{589}$ +43.0° (MeOH)



Ic $[\alpha]_{589}$ +184° (MeOH)

Supposing that the puckering mode of each five-membered ring in **Ia**, **Ib**, and **Ic** is almost the same as that in **II**, the possible octant projection are given in Figure 3A (M-helicity) and 3B (P-helicity) for the rings of **Ia** and **Ic**, respectively, when *t*-butyl groups assume quasi-equatorial orientations. Non-C_2 symmetrical **Ib** is composed of P- and M-helicity rings. Then the observed c.d. signs (negative for **Ia** and positive for **Ic**) seem to be considerably contributed by the chirality of five-membered rings.

However, the effect of interaction between two carbonyl groups is also pronounced, as is shown by the large difference in the absolute value of rotational strength between **Ia** and **Ic**,

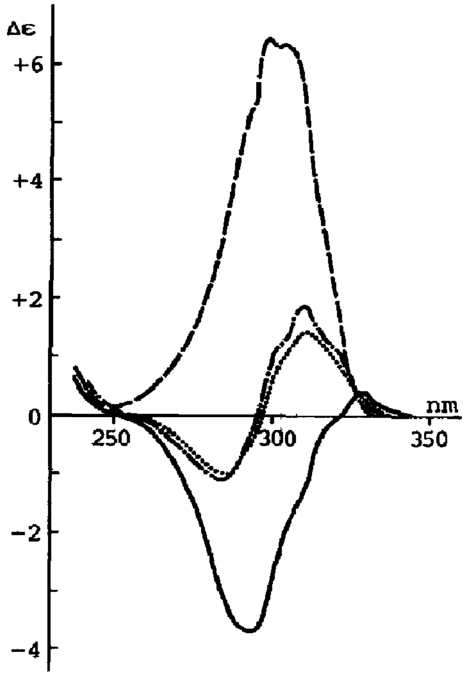


Figure 1. C.d. spectra of (−)-**Ia** (———), (+)-**Ib** (-·-·-), (+)-**Ic** (-----), and (+)-**II** (·········) in methanol.

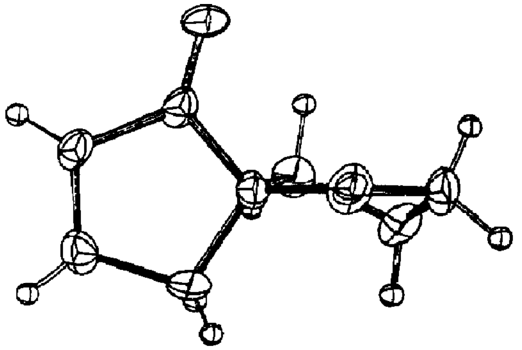


Figure 2. Octant projection of (*R*)-**II** determined by X-ray analysis.$^{3)}$

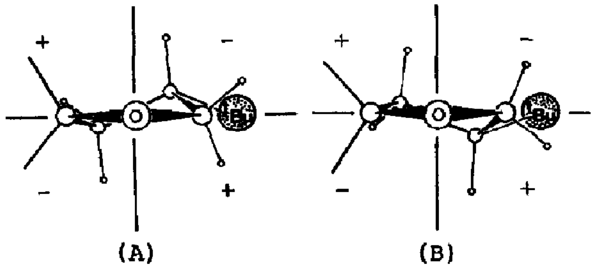


Figure 3. One of the possible octant projecti of (*3S*)-ring (A) and (*3R*)-ring (B).

as well as by the bisignate feature of **Ib** in which the contributions by two skeletons should be approximately cancelled out and the effect of interaction between carbonyls predominant.

In addition, the large difference between the c.d. spectra of **Ic** and **II** is striking since they are assumed to have almost the same skeletal arrangement as shown in Figure 2 and 3B. The c.d. feature of **II** is rather similar to that of non-symmetrical **Ib**, and their similarity was also observed in EPA solution (ether-isopentane-ethanol 5:5:2) at low temperatures. Hence the conformation of **II** can be considered rather flexible and, in solution, may not necessarily resemble that revealed by X-ray study.$^{4)}$

The exact evaluation of the individual contributions by ring chirality and interaction between two carbonyls in these diones is not easy at present, and the study on this point is now in progress. The more detailed results of c.d. measurement will be reported in the near future.

References and Notes

1) M. Sumiyoshi, H. Kuritani, K. Shingu, and M. Nakagawa, *Tetrahedron Lett.*, 1243 (1980).
2) 1,6-Dimethylene-3,8-di-*t*-butylspiro[4.4]nonane from **Ic** was analysed by Drs. Nakai and Shiro in Shionogi Research Laboratory.
3) C. Altona, R. A. G. DeGraaff, C. H. Leeuvestein, and C. Romers, *Chem. Comm.*, 1305 (1971).
4) *cf.*, D. A. Lightner, G. D. Christiansen, and J. L. Melquist, *Tetrahedron Lett.*, 2045 (1972).

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