

*Stability Sequence of Five Stereoisomeric Perhydro-1 : 4-dioxophenanthrenes.*

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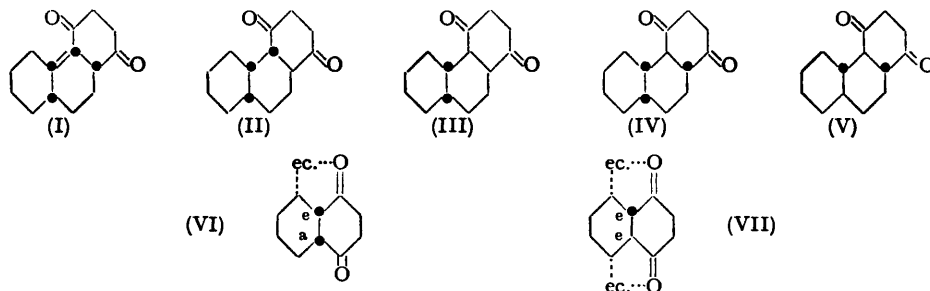
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A quasi-theoretical stability sequence for five stereoisomeric perhydro-1 : 4-dioxophenanthrenes is shown to agree well with the experimentally established stability sequence if a value of *ca.* 2 kcal./mole is assigned to the energy increment due to the non-bonded interaction between the oxygen atom of a carbonyl group and a  $\beta$ -situated carbon atom in an eclipsed (equatorial) position.

IN a previous communication (Robins and Walker, *J.*, 1954, 3960) we described the preparation, starting from the stereochemically labile *cis-syn- $\Delta^{9:14}$* -dodecahydro-1 : 4-dioxophenanthrene, of a series of five perhydro-1 : 4-dioxophenanthrenes (I—V). Interconversions by way of characterised intermediates, involving selective methods of reduction and oxidation together with controlled stereochemical inversions at points of ring fusion rendered labile by the presence of adjacent carbonyl groups, enabled a logical assignment of structures to be made to these stereoisomers, and provided experimental evidence for the following stability sequence for the five perhydro-1 : 4-dioxophenanthrenes: *trans-anti-trans* (V) > *trans-syn-cis* (II) > *cis-anti-cis* (III) > *trans-anti-cis* (IV) > *cis-syn-cis* (I). This sequence differs from the stability sequence for the parent perhydrophenanthrenes postulated by Johnson (*Experientia*, 1951, 7, 315), namely: *trans-anti-trans* > *trans-syn-cis* = *trans-anti-cis* > *cis-anti-cis* > *cis-syn-cis*, to which that author later (*J. Amer. Chem. Soc.*, 1953, 75, 1498) assigned energy differences as follows: *trans-anti-trans*, 0; *trans-syn-cis* and *trans-anti-cis*, 2.4 kcal./mole; *cis-anti-cis*, 4.0 kcal./mole; and *cis-syn-cis*, *ca.* 6.4 kcal./mole. The reason for the apparently greater *relative* stability of *cis-anti-cis*-perhydro-1 : 4-dioxophenanthrene (III) as compared with the parent hydrocarbon must be

sought in a factor, or factors, introduced by the carbonyl groups, and it is the object of the present communication to offer an explanation.

When a 1 : 4-dioxocyclohexane ring is fused with another cyclohexane ring, both being chair forms, a *cis*-fusion (VI) introduces *one* eclipsed configuration (ec.) between the oxygen atom of a carbonyl group and a  $\beta$ -situated equatorial carbon atom contained in the other ring, and a *trans*-fusion (VII) introduces *two* such eclipsed configurations. In this way



it can be seen that the presence of the carbonyl groups has a smaller effect in reducing stability when a 1 : 4-dioxocyclohexane is fused with a cyclohexane ring in the *cis*-position than when fusion occurs in the *trans*-position, since the greater stability of the *trans*-form of the carbon skeleton is offset by the energy increment for an extra eclipsed O<sup>+</sup>-C non-bonded interaction. The value of this energy increment can be estimated to be between 1.6 and 2.4 kcal./mole as follows. *trans-anti-trans*-Perhydro-1 : 4-dioxophenanthrene (V) was shown to be completely unaffected by conditions likely to effect its conversion into either *cis-syn-trans*- or *cis-anti-trans*-perhydro-1 : 4-dioxophenanthrene, so that the requisite energy uptake by the carbon skeleton (2.4 kcal./mole) in such a change must exceed the loss due to removal of one O<sup>+</sup>-C eclipsed non-bonded interaction; this value, 2.4 kcal./mole, may therefore be regarded as the upper limit for the energy increment for an eclipsed O<sup>+</sup>-C non-bonded interaction. On the other hand *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (IV) was shown to undergo substantial conversion into a mixture of *cis-anti-cis*- (III) and *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (II); (II) and (IV) are of equal energy content both as regards their carbon skeletons and in each having *two* O<sup>+</sup>-C eclipsed non-bonded interactions, but the formation of (III) from (IV) involves the addition of 1.6 kcal./mole to the energy of the carbon skeleton and the loss of *one* eclipsed O<sup>+</sup>-C non-bonded interaction, so that a lower limit of 1.6 kcal./mole may be set to the energy increment due to the latter. If we therefore take the energy increment for the O<sup>+</sup>-C eclipsed non-bonded interaction as 2 kcal./mole we may derive a quasi-theoretical stability sequence for our five stereoisomeric perhydro-1 : 4-dioxophenanthrenes as shown in the Table.

*Energy differences of perhydro-1 : 4-dioxophenanthrenes.*

	Energy differences due to carbon skeletons * (kcal./mole)	Energy increments on account of eclipsed O <sup>+</sup> -C non-bonded interaction(s) (kcal./mole)	Net energy differences (kcal./mole)
<i>trans-anti-trans</i> (V)	0	4	0
<i>trans-syn-cis</i> (II) ...	2.4	4	2.4
<i>trans-anti-cis</i> (IV)...	2.4	4	2.4
<i>cis-anti-cis</i> (III) ...	4.0	2	2.0
<i>cis-syn-cis</i> (I).....	ca. 6.4	2	ca. 4.4

\* From Johnson (*J. Amer. Chem. Soc.*, 1953, **75**, 1498).

The "theoretical" order of stability for the five stereoisomeric perhydro-1 : 4-dioxophenanthrenes is therefore now seen to show satisfactory agreement with the experimentally established sequence.