Violation of Kruszewski's Rule

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Violations of Kruszewski's rule occur in the case of the annelation of $(4\,m)$-membered rings, provided m is sufficiently large. In many cases the violation starts even with $m = 2$.

Recently Kruszewski [1] proposed an empirical rule for predicting the relative stability of conjugated isomers obtained by attaching a six- or a four-membered ring to different positions of the parent molecule. Since the effect considered by Kruszewski is obviously closely connected with cyclic conjugation [2], it was reasonable to expect that his observation is a special case of a more general modulo 4 type rule. In [3] this rule has been formulated as follows:

(a) If $n = 4\,m + 2$, then

$$p_{rs} > p_{tu} \Leftrightarrow E(B_1) > E(B_2)\,.$$

(b) If $n = 4\,m$, then

$$p_{rs} > p_{tu} \Leftrightarrow E(B_1) < E(B_2)\,.$$

(Here and later we use a symbolism which fully coincides with the notation in [3], where the reader may find the necessary details.) In [3] Kruszewski's rule (a) was rigorously proved. A detailed analysis showed, however, that rule (b) can not be generally valid. Qualitative arguments supported the validity of (b) for $m = 1$, indicating also that violations of rule (b) can occur for larger values of m. In fact, if $n = 4\,m$, then Eq. (5) in [3] can be written as

$$E(B_1) - E(B_2) = I_1 + I_2\,,$$

where

$$I_1 = \frac{2}{\pi}\int_0^{x_0} \log \frac{Q_n - |R_n|(A - v_r - v_s)}{Q_n - |R_n|(A - v_t - v_u)}\,dx\,,$$

$$I_2 = \frac{2}{\pi}\int_{x_0}^{\infty} \log \frac{Q_n + |R_n|(A - v_r - v_s)}{Q_n + |R_n|(A - v_t - v_u)}\,dx\,.$$

The parameter x_0 is the (unique) real and positive zero of the polynomial R_n, that is, x_0 is the root of the equation

$$(P_{n-2}) = 2\,.$$

Since

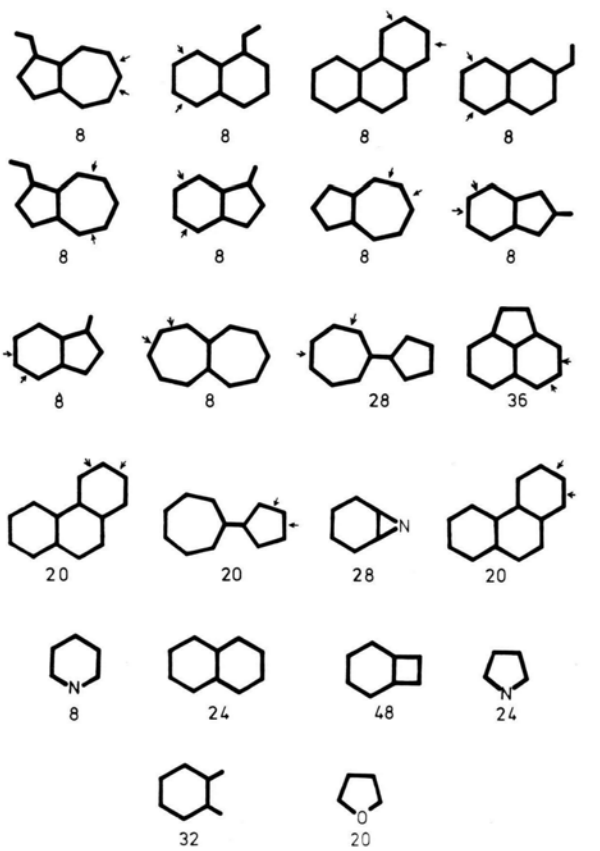
$$(P_{n-2}) = \sum_{k=0}^{(n/2)-1} \binom{n-2-k}{k} x^{n-2-2k}$$

$$= 1 + \frac{n(n-2)}{8}\,x^2 + \ldots + x^{n-2}\,,$$

a good approximation for x_0 is

$$x_0 \approx \sqrt{\frac{8}{n(n-2)}}\,.$$

It has been demonstrated [3] that the dependence of the first integral, I_1, on molecular topology is in agreement with rule (b). The contribution of the second integral, I_2, however, is opposite to



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Kruszewski's predictions. Whether Kruszewski's rule (b) will hold or not, depends on the relative magnitude of the integrals I_1 and I_2. When n is (relatively) small and thus x_0 (relatively) large, the effect of I_1 will dominate. With increasing n, the effect of I_2 will become more and more important since x_0 and therefore also I_1 will tend to zero. Thus one can expect that if n is above a certain critical value, n_{crit}, the inversion of Kruszewski's rule (b) will occur:

(c) If $n = 4m$ and $n \geqq n_{crit}$, then

$$p_{rs} > p_{tu} \Leftrightarrow E(B_1) > E(B_2) .$$

In Fig. 1 various conjugated systems, together with the computed value for n_{crit} are presented. The following observations are worth mentioning.

1. An inversion of rule (b) to rule (c) was found in all studied cases. 2. Violations of Kruszewski's rule (b) have never been observed for $n = 4$. On the other hand, in a considerable number of cases the inversion starts with 8-membered rings. 3. A remarkable finding is that n_{crit} has either the value 8 or is very large and chemically insignificant ($n_{crit} \geqq 20$). Intermediate n_{crit} values seem to be rather rare. 4. No reasonable quantitative relation could be recognized between n_{crit} and the difference between the corresponding bond orders of the parent compound. 5. On the other hand, small n_{crit} values usually occur if the two (nonequivalent) bonds on which the annelation effect was compared have similar topology and consequently have nearly equal bond orders.

This latter observation suggests that irrespective of certain limitations, Kruszewski's rule can be used as a simple qualitative scheme for guessing the relative thermodynamic stability of isomeric conjugated molecules.

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