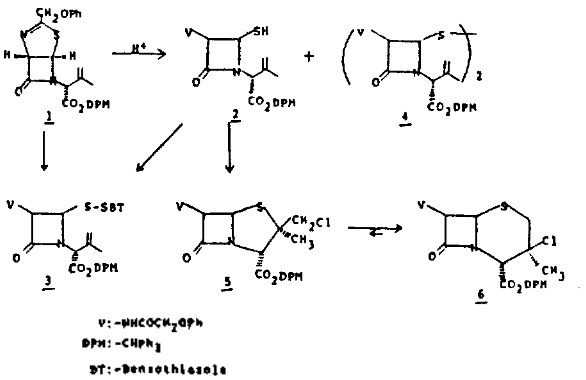
ing benzoyl peroxide was not observed.

The ring closure of mercaptan **2** took place with t-BuOCl. Treatment of the mercaptan with t-BuOCl in CCl_4 resulted in chloromethylpenam **5**.[11] When heating in dimethylsulfoxide[12] at 100°, penam **5** was converted to chlorocepham **6**.[11]

Dimer **4** was also the by-product in the reaction with *t*-BuOCl. The reaction gave only the kinetic product,[5,12] the penam. A similar result was obtained by treatment with N-bromosuccinimide or other positive halogen precursors.



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Missing Terms in Semiempirical Evaluation of Molecular Properties

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When molecular properties (meaning electric or magnetic properties which molecules exhibit under the influence of electric or magnetic field) within valence space are desired, the total hamiltonian (H) should be transformed to an effective valence shell Hamiltonian (H^{eff}). H^{eff} acts only within a valence space (P space). In our early work[1], we showed a formal derivation of H^{eff} for properties. That is,

$$H = H^{o} + \lambda M \tag{1}$$

$$H^{eff} C_P = (E^{o} + \lambda E')C_P \tag{2}$$

$$H^{eff} = H^{o,eff} + \lambda M^{eff} - \lambda H^{o}_{PQ}(E^{o}_{QQ} - H^{o}_{QQ})^{-1} E'_{QQ} (E^{o}_{QQ} - H^{o}_{QQ})^{-1} H^{o}_{QP} \tag{3}$$

$$H^{o,eff} C^{o}_P = E^{o} C^{o}_P \tag{4}$$

$$H^{o,eff} = H^{o}_{PP} + H^{o}_{PQ}(E^{o}_{QQ} - H^{o}_{QQ})^{-1} H^{o}_{QP} \tag{5}$$

$$\begin{aligned} M^{eff} = M_{PP} &+ M_{PQ}(E^{o}_{QQ} - H^{o}_{QQ})^{-1} H^{o}_{QP} \\ &+ H^{o}_{PQ}(E^{o}_{QQ} - H^{o}_{QQ})^{-1} M_{QP} \\ &+ H^{o}_{PQ}(E^{o}_{QQ} - H^{o}_{QQ})^{-1} M_{QQ} (E^{o}_{QQ} - H^{o}_{QQ})^{-1} H^{o}_{QP} \end{aligned} \tag{6}$$

where H^{o} is molecular electronic Hamiltonian, M is property operator (external field), C_P is true valence wavefunctions in matrix form, E^{o} is molecular energy, and E′ is molecular property value. P denotes a valence space and Q denotes a complementary space. H_{PQ}, H^{o}_{PQ}, M_{PQ} etc. are matrix elements of operators H, H^{o}, M etc. between the state in P space and that in Q space, respectively. The superscript eff means that the operator (H, H^{o} or M) is transformed into effective one. λ is an expansion index.

Semiempirical Hamiltonians consider valence electrons only, which suggests that the semiempirical Hamiltonian (H′)

is a model Hamiltonian of true effective Hamiltonian (H^{eff} or $H^{o\text{-}eff}$)[2]. In the absence of external field,

$$H^s C_P^o = E^o C_P^o \tag{7}$$

In semiempirical methods, the necessary matrix elements are not theoretically evaluated, but rather obtained from suitable experimental values.[3]

When a dipole moment is desired, M in equation (1) becomes a dipole moment operator. In semiempirical methods, the above equation (7) is solved to obtain valence wavefunctions C_P^o. And dipole moment between the state $C_{P,i}^o$ and $C_{P,j}^o$ is evaluated as $C_{P,i}^{o*} M C_{P,j}^o$. Since dipole moment is the first order property, the use of C_P^o instead of C_P does not cause a significant error. However, by inspecting the equation (3), we can easily find that the last term is conveniently *neglected*. The last term in equation (3) represents the molecular energy level shift due to the interaction between dipole moment operator and molecular electronic Hamiltonian.

Now let us examine the second order property, for example, magnetic susceptibility. In this case, the property operator M is a magnetic field. Pascal's rule says that molecular susceptibility is **not** simply a sum of atomic susceptibilities. It implies that the semiempirical Hamiltonian, H' should be modified to include magnetic field effect besides molecular energy.[4] In semiempirical methods, the H' is actually altered to take in the external field. And, consequently, modified valence wavefunctions (equivalent to C_P of equation (2)) are utilized to calculate the magnetic susceptibility. However, since experimental data for susceptibilities are so scarce, there are no simple ways of determining matrix elements of H^{eff} from experiments. To avoid this difficulty, matrix elements of H^{eff} (exactly speaking matrix elements of M^{eff}) are theoretically calculated in an approximate manner. Apart from the approximation, there is an intrinsic inconsistency in it.

As methioned before, H^s is a model form of $H^{o\text{-}eff}$ when only molecular energy is considered. When molecular property is desired, H' should be a model form of H^{eff}. When the modelled H^s is solved for energy, in semiempirical methods, **all** the correlation energy is supposed to be included into it. This is done via taking matrix elements of H' from experiments. In semiempirically determining H^{eff}, the matrix elements of M^{eff} are theoretically evaluated — it means that the last three terms in right hand side of equation (6) are neglected. The correlation part of M^{eff} **is not** included into H', but the correlation part of $H^{o\text{-}eff}$ **is** included into H^s. Though these errors may be small enough within chemical accuracy, the formal justification of semiempirical way of determining molecular properties might well be reinvestigated.

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