Does the Clar rule work in cyclic π–electron systems with the intramolecular hydrogen or lithium bond?

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The Clar rule[1] states that many physicochemical properties of polycyclic aromatic hydrocarbons may be well understood in terms of the localization of the aromatic sextet present in the molecule. The idea is to assign the π–electrons that can participate in aromatic sextets to particular rings and to do so in such a way as to obtain the maximum number of π–electron sextets. In this way, π–electron delocalization of a particular ring within a benzenoid hydrocarbon is qualified by the Clar rule as (i) the 'empty' ring, as in the case of central ring in triphenylene, or (ii) containing localized double bond(s), as in the case of the central ring in phenanthrene and alike, or (iii) containing a localized or migrating aromatic sextet, as in triphenylene or naphthalene. Properties of individual rings may be quantified in terms of the magnitude of aromaticity indexes.[2]

Application of the geometry based index HOMA[3] and magnetism based index NICS[4] as well as energies of bond separation reactions[5] allow to show that replacement of CHCHCH fragments in benzenoid hydrocarbon π–electron system by O…H…O or O…Li…O or O…H…N or O…Li…N fragments still lead to a possibility of application the Clar rule to these modified systems. The Li-bonded systems exhibit better similarity to the benzenoid systems than H-bonded ones.[6]

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