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Aromaticity of heterocyclic compounds pdf

Flavourings from five heterocyccal elements containing up to three heteroatoms are quantified by the dimethydide hydroprene (DHP) probe. The fixation of bonds due to the fusion of heterocycles with dimethyldihydropiyrene nucleus (DHPN) was measured by changes in chemical changes in 1H NMR (magnetic) and binding length (structural criterion). Chemical changes in dihydropyrene are calculated in GIAO HF/6-31G(d)//B3LYP/6-31+G(d). In the case of chemical change analysis 1H NMR, two non-aromatic reference models are tested. Among the heterocycles studied, pyrazole and triazole are 80-85% aromatic compared to benzene, both by magnetic and geometric criteria. Thiazole and oxazoles are the least aromatic, where quantitative aromatic estimates are about 34-42%, compared to benzene. These quantitative estimates of the flavourings of the five member heterocycles are also comparable to those of aromatic stabilisation sources. Quantification of aromatics through energy, magnetic and structural criteria may provide similar conclusions, provided that appropriate reference systems are selected.1. IntroductionAromaticity is a basic and widely used concept in chemistry. Aromaticity is commonly understood by the Convention because it is not a directly measurable quantity. Qualitatively, the compound can easily be classified as aromatic, nonaromatic, or anti-aromatic. However, the quantification of the degree of aromaticity has become very controversial. Many methods of quantifying aromatics have appeared in the literature since Kekulé introduced this concept [1]. However, no single method can gain universal acceptance. Our perception of the aromaticity of a compound may vary considerably depending on the method chosen for quantitative analysis [2]. Each method chosen for the quantification of aromatics is essentially based on a single criterion (3), whereas aromaticity is multidimensional (consisting of energy, magnetic and structural components). Aromaticity gives some additional stability to aromatic compounds compared to the non-aromatic compound of the reference model. Therefore, aromatic stabilisation energy (based on homodesmotic reaction [4, 5]) is often considered to be the main criterion for the reactivity of aromatic compounds [6, 7]. A number of other stabilisation energy sources reported in the literature to take account of this additional stability are Hessa-Schaad resonant energy [8-13], Huckel resonance energy [14-16], Schleyer isomer stabilization energy [17], Dewar resonance energy [18-21] and topological resonance energy [22-24]. Among the structural criteria, the model of the harmonic aromatic oscillator (HOMA) [25-27] is a common method of estimating aromatic characteristics. The literature [28-35] also contains several other structure-based criteria[28-28]. The third category of aromatic quantification methods is based on the Magnetic. Magnetic criterion quantification includes magnetic sensitivity exaltation [36-47], magnetic sensitivity anisotropy, NMR (chemical changes and continuous coupling analysis) [42, 48-54] and independent chemical change (NICS) [55]. In the analysis of chemical change, the atom of interest over the aromatic nuclei is covalently or artificially placed (through non-covalent interactions). The latter includes the nuclei 3He and 9Li located above the aromatic nucleus [42, 48–54], while the former include a 1H chemical displacement [56,57] analysis of the probe protons, usually at the centre of the nucleus under consideration. The probe molecule for chemical change analysis 1H must meet the following two requirements: (i) the annular current in the probe molecule affects only the deposition of electrons and (ii) by anisotropic action in space should not affect the chemical shifts of the probe protons. 15,16-Dimethyldihydropyrene 1 (Figure 1) is an excellent probe molecule in this respect. The internal methyl protons in dihydropiren are strongly sheltered due to the diatropic annuities current (by 5.2 ppm), compared to the uncoorated model 2, and [a] or [e] the merger of arenas to the nucleus of dihydropyrene reduces the annuities current of the dihydropiyren nucleus. This reduction in annuity current is proportional to the aromatics of the combined arenas. A very aromatic arena will result in a much greater reduction in ring current and vice versa. For example, the fusion of a benzene ring with DHPN (3) results in 58% bond fixing, while a less aromatic octopus[14] annulene (in 4) results in 30% bond fixing [57]. The fusion of the arena with DHP not only changes the ring current dhpn (vide supra), but also affects the geometric parameters. Therefore, the results of the magnetic criterion (NMR) can be easily correlated with geometric parameters (binding fixation). The dimethylsihydropyrene probe has been successfully used to quantify the aromatics of many otons, including polycyclic aromatic hydrocarbons [56] and heteroarenes. Recently, we have successfully applied dhpn chemical change analysis to quantified the aromas of six member nitrogens containing heterocycles (asins) [58]. For example, dhp 5 melted azaine is used to quantify the aromaticity of pyridine. In this work, we are expanding our recently developed approach to the aromatic quantification of the five member heterocycles. Two different non-aromatic reference models are tested for aromatic quantification and the results are compared with the binding values obtained from the structural criterion. Moreover, the results are compared with HOMA and ASE for these heterocycles.2. Results and discussions2.1. Selection of the reference systemIn our recent study on the quantification of the aromaticity of azines [58], the choice of the appropriate reference model is shown to play a very key role due to the anisotropic effect [60], resulting from heteroatoms. We 've had the different non-aromatic models (shown below in Figure 3) and the best non-aromatic model for a reliable estimation of aromatic quantity is a model with partial ins saturation of azane (pyridine). The partially saturated non-aromatic reference model (7) is very similar to the azane tested, except that it lacks the aromaticity of azaine. Compound 8 was used as an unconnected reference model for the quantification of aromatics; however, compound 2 may also be used with little effect on the results (Figure 2). The importance of choosing the appropriate reference model was also noted during the quantification of the aromatity of cycloceanone 9 [61]. Cyclopentadiene fused DHP (10) was a more reliable reference model than dhp cyclopentanone 11.2.2. Parent DHP as reference modelIn the last three decades, dihydropyrene has emerged as an excellent probe for quantifying aromatics [56, 61]. In general, the change in DHPN annuities by merming from the arena is described by the change in the chemical shift of the internal protons in relation to the parent DHP 1 (DHP 1 is the reference model). For example, the change in the annuation current of the dihydropyrene nucleus (DHPN) in fusion with heterocycler (pyrrole) is as follows: The above equation is in fact a measure of binding in the nucleus of dimethylihydropyrene by fusion with aromatic apricot. On the basis of the above formula, the aromaticity of arenas (pyrrole) in relation to benzene can be estimated bythis approach has succeeded in quantifying the aromaticity of carbocicles such as benzene, naphthalene, anthracene [56], cyclopentadiene [61], and cyclooctatetraene [62] (vide supra). Heterocycles present additional effects of anisotropy as well as potential conjugation effects, therefore, have not been extensively studied to quantify aromatics using the DHP probe. For such instances, parent DHP 1 cannot be used as a better reference model compound; therefore, the reference model and equations for calculating aromaticity are modified. The reduction in the relocation of pyroprorole melted DHP 12 through reference model 14 can be calculated using pyrolysis oscalculability in relation to benzene can be calculated chemical shifts of methylprotons into nonconjug models (5 and 16) do not differ too much from chemical shifts of similar protons in 2 [58] and it is expected that that chemical shifts of internal protons 13 will also not differ significantly. Indeed, internal methyl protons in 13 appear in 1.14 compared to 1.12 for 2. With these approximations (4), you can modify to (5). In this study (2) and (5) they are used to quantify the aromatics of the five member heterocycles.2.3. Calculation methodsAll calculations were made from gaussian 09 program package [63]. Structure geometries have been optimized without any symmetry constraints with the B3LYP hybrid method using the 6-31+G base set* B3LYP B3LYP method of becke's three hybrid functional parameters [65] in combination with the functional correlation of Lee et al. [66]. The B3LYP method strikes a nice balance between cost and accuracy and is known to work very well to predict the geometry of many dihydropyrenes [67]. Each optimized structure has been confirmed by a frequency analysis at the same level (B3LYP/6-31+G(d)) as a true minimum (no imaginary frequency). Chemical changes of 1H NMR were calculated using an independent atomic orbital (GIAO) method based on 6-31G* set on optimized B3LYP/6-31+G(d) geometry (GIAO-HF/6-31G(d)/B3LYP/6-31+G** GIAO-HF/6-31G* was selected, because the predicted aromatics of many dihydropyrenes using this method correlate very well with the experiment [68]. The three hydrogens in the methyl group seemed different due to their constant positions in magnetically different environments. The reported values are averaged chemical changes.2.3.1. Five Members of Heteroatomic RingsPyrrole can be combined with DHP in two different ways to supply dihydropyrene 12 and 17 (Figure 4). We have shown before that isosric fusion of heteroarene (azyne) into DHPN can provide a slightly different estimate of aromaticity, even if there is a complete relocation in each fragment. However, if the relocation in one fragment is blocked by the second fragment, the estimation of the aromaticity is not reliable. The fusion of pyrolysis with dhp fragment in 12 allows for a level playing field for the π in each fragment; however, the situation is different in the 17th The fusion of pyrrole to DHPN in 17 causes an almost complete loss of dhpn (vide infra) nucleus aromaticity, as the π electronic cloud is not available for relocation to DHPN. Therefore, compound 12 is ideal for estimating the aromaticity of pyrrole. Internal methyl protons in 12 appear at −3.31 for both methyl groups, indicating that the anisotropic effect resulting from nitrogen is insignificant or very similar for both methyl groups. Internal methyl protons in 2 are calculated at 1.12. Therefore, internal protons in 12 are shielded only by 4.43 ppm, compared to 7.40 ppm for native DHP 1 (−6.29). DHPN in DHP 12 pyrrole retains about 59.8% of its aromaticity, which means that the pyrrole ring results in 40.2% bond fixing in DHPN. This bond fixation is relatively small compared to 58.9% of bond fixing caused by the benzene ring (see Table 1 for details). The relative aromaticity of pyrolysis to benzene, calculated by (2), is 68.2%. It is important to mention that experimental chemical changes are available for BENZO DHP 3; however, to maintain consistency, theoretical values are used for mate calculations in this study. The higher aromaticity of benzene can be rationalised by the Clara rule (69). EntryHeterocyclesDHPδ% bond fixing% aromaticity (relative to benzene)1 1-6,29 internal methyl protons in isose 17 appear at −0.31, indicating that the pyrolysis ring in this fusion caused an almost complete loss of DHPN aromaticity (as expected). Similar behavior is also observed in tiofen melted dihydropyrenes 18 and 19. Internal protons in 19 appear at 0.24 compared to −4.16 for 18. The binding fixation caused by the thiofen ring at 18 is 28.9%, indicating that the thiofen ring is only 48.9% aromatic compared to benzene. Among heterocycles with two heteroaths, octave (20), isoxazole (21), thiazole (22), isothiazole (23), pirazole (24) and imidazole (25) are tested for quantification of aromaticity (Figure 5). Isoxazole causes more binding fixings in DHPN than oxazole (Table 1, entries 5 and 6). The flavors of oxazole and isoxazole, relative to benzene, are 34 and 63.5%, respectively. A similar trend of aromatization is observed in thiazole and isothiazole with dihydropirenes (22 and 23). The percentage of thiazole and isothiazole flavourings in relation to benzene is 38,9 and 58,9 % respectively (Table 1, Headings 7 and 8). The aromaticity of thiazole is relatively high compared to oxazole, while the aromaticity of isothiazole is less than isoxazole. The aromaticity of pyrazole 24 (86% relative to benzene) is higher than iso-marine imidazole 25.Among heterocycles with three heteroaths, oxadiazole (26) and triazole (27) are studied. The latter results in a greater reduction in ring current (48%) downfield signal of −2.91. The aromaticity of triasaol is 82% compared to benzene, and this is very comparable to pyrazole. Internal methyl protons in oksadiazoles are simulated at −3.59, indicating 62% aromaticity compared to benzene.2.4. Non-aromatic model with HeteroatomNext, the relative aromas of these heterocycles are estimated using a saturated reference model (14, 28-36). The reference models are very similar to the watered dihydropyrenes 12, 17 to 27, except that heterocycles do not have flavours. For example, the reference models for dhp 12 melted pyrolysis are dhp 14 melted pyrrolidine. Similarly, the saturated reference model for the 18 is 28. Suitable saturated reference −5.4553.91003Pyrrole12−3.3114−5.6234.363.64Thiophene18−4.1628−6.0826.949.55Oxazole20−4.829−5.8815.428.66Isoxazole21−3.5130−5.6531.658.97Thiazole22−4.5931−5.9819.636.38Isothiazole23−3.9932−6.0531.558.59Pyrazole24−2.5233−5.8948.189.210Imidazole25−3.8134−5.5125.649.611Oxadiazole26−3.5935−5.6330.556.612Triazole27−2.9136−5.8344.983.3The data in Table 2 reveal that the estimates of aromaticities using the nonaromatic reference models 14, 28–38 (through (5), shown in Table 2) are very similar to from (2) (Table 1) when the parent DHP is used as a reference). For example, the aromaticity of pirroli relative to benzene is 68% (to (2)) compared to 64% for the use of (5) quantification of aromatics. In the case of thiofen, the difference in aromatherapy measured by two different methods is even smaller; 48.9% (2) compared to 49.5% (5). The difference in aromatic percentages from benzene is 5 % (for both methods) for most heterocycles, except that imidazole melted DHP 25, where 56,9 % and 49,6 % of aromaticity are estimated in relation to benzene by (2) and (5), respectively. Although both methods provide comparable aromatic estimates with the exception of imidazole and oxazole, this reflects that the anisotropic effect of heteroathom is very insignificant for chemical shifts of internal DHPN methyl protons. Furthermore, this is also confirmed by the fact that the two internal methyl protons in dihydropirenes 12, 17 to 25 show similar chemical changes (within 0,02 ppm units). However, geometrical parameters were also examined in order to further confirm which of the abovementioned methods is more accurate with regard to aromatic estimates. Fixing bonds in DHPN also changes the length of DHPN bonds. The degree of change in the length of the DHPN bundles should also reflect the aromaticity of the combined arena. The results of the geometric analysis are given in Table 3 (for the numbering scheme, see Figure 7). Analyses of geometric data show that the aromaticity of imidazole in relation to benzene is 59%, which is very similar to the aromatic values from 56.9% to (2) (magnetic criteria). Similarly, the aromatic value of oxadiazole by geometric criteria is 62,9 % relative to benzene, which is again in line with the value obtained by (2) (magnetic criteria). In general, the results of geometric criteria are very comparable to those of (2) (when parent DHP 1 is the reference model). 3121820212223242526 27C1-C21.396 1.384 1.388 1.391 1.385 1.39 1.386 1.381 1.389 1.386 1.382 C2-C31.4191.4121.4081.4061.4121.4091.411.4161.4111.4161.416C3-C41.382 1.388 1.391 1.394 1.389 1.393 1.39 1.385 1.39 1.39 1.386 C4-C51.4191.4151.411.4091.4131.4091.4121.41961.4131.4131.419C5-C61.382 1.388 1.391 1.394 1.389 1.393 1.39 1.385 1.39 1.39 1.386 C6-C71.4191.4121.4091.4061.4111.4061.4091.4161.411.411.415C7-C81.399 1.385 1.389 1.3923 1.388 1.391 1.388 1.382 1.389 1.3866 1.382 C8-C91.42961.421.4141.4131.4191.4131.4191.4251.4191.4181.4245C9-C101.393 1.398 1.382 1.383 1.398 1.384 1.38 1.393 1.399 1.398 1.393 C10-C111.4541.4191.4151.4001.411.4121.4191.4241.4131.411.421C11-C121.435 1.419 1.419 1.4 1.3986 1.416 1.413 1.414 1.412 1.4 1.4065 C12-C131.4541.4261.4291.41241.4231.421.4281.4291.4191.4191.425C13-C141.393 1.396 1.38 1.38 1.396 1.381 1.399 1.393 1.399 1.395 1.391 C14-C11.4281.4211.4191.4151.4211.4151.4191.4251.4191.4211.425Av (bold italic)1.4311.41961.1 4141.40881.41561.411191.4161.42181.41491.41511.4205Bav (italics)1.385 1.3883 1.4391 1.3906 1.3926 1.3894 1.3848 1.3889 1.3865 1.3865 Bond fixing (Aav − Bav)0.04540.02930.02290.01820.02940.01910.02660.0390.02590.02860 0369% arom.100.064.550.340.164.642.258.581.659.162.980.9 The results here are our recent studies in which we have shown that these saturated reference models containing heteroaatoms provide better flavouring estimates. An anisotropic effect may be present in the saturated reference model, leading to unreliable aromatic estimates for these heterocycles. Because both geometric and magnetic (NMR) based methods, in this study, provide similar conclusions about the aromatic five members of heterocycles; therefore, we are not only confident in the reliability of the results, but also show that different aromatic criteria can provide the same information if a suitable model system is chosen. We also compared the results obtained here with the aromatic values of the literature for these heterocycles using other methods [70] (Table 4). The comparison of the results clearly shows that the results here are very comparable to the value of aromatic stabilisation energy. For example, ase pyrrole is higher than thiofen (20.59 compared to 18.59), indicating that the pyrolytic ring is more aromatic than thiofen. This is in line with our calculations that higher bond bond binding is observed caused by pyrorols than thiofen. Moreover, oxazole (Table 4 Record 3) has an even lower ASE, which is consistent with our results here that the binding fixation caused by oxazole is lower than both thiofene and pyrrole. Among these heterocycles, the highest ASE is for 1,2,3 triasine (26,66), followed by pyrazole (23,9). It is worth noting that triazole and pirazole are heterocycles that exhibit the highest bond fixing in DHPN. PpmASE'sNICSHOMAGeom molecule. NMRPyrrole 2.0420.59−10.600.49364.568.1Cut 2.3918.59−10,990,99950.348.9Oxazole 2.1512.39 −9 9.450.0840.134.1Isoxazole 1.9919.29-10.580.26164.663.5Thiazole 2.5419.43−11.390.92942.2 38.9Isothiazole 2.6320.18−11.660.99458.559.1Pyrazole2.2923.9−11.930.82181.686.1Imidazole2.2918.. 98-10.830.81159.156.91,2,3-Triazole 2.9226.66−13.610.81980.981.8 We also associated our results with HOMA values [71]. Trends in the estimation of relative aromas are very similar in the heterocycle series. For example, both HOMA and NMR provide the same trends in aromatic azoles: pyrazole aromatics > triazole > imidazole. There are some differences when two different series of heterocycles are studied (thiofen and pyrolysis). With this comparison, we have shown that geometric, magnetic (this work) and energetic (literature) aromatic criteria can provide the same trend in arena flavourings, provided that an appropriate system is chosen. This further confirms the potential of DHPN in quantifying the aromaticity of heteroarene.3. Aromatic conclusions of five member heterocicles containing up to three heteroatomes are (DHP). The fixation of bonds due to the fusion of heterocyclic with dimethyldihydropiren nucleus (DHPN) was measured by changes in chemical changes in 1H NMR (magnetic) and binding length (structural criterion). Chemical change data for dihydropyrenes are calculated in GIAO HF/6-31G(d)//B3LYP/6-31+G(d). In the case of chemical change analysis 1H NMR, two non-aromatic reference models are tested. Parent DHP serves a better reference model for aromatic quantifications. These heterocycles aromas are descried in relation to benzene. Among the heterocycles studied, pyrazole and triazole are the most aromatic, which are about 80-85% aromatic relative to benzene, both by magnetic and geometric criteria. On the other hand, thiazole and oxazoles are the least aromatic, where quantitative aromatic estimates are about 34-42% compared to benzene. Quantitative estimates of aromas through magnetic (2) and geometric parameters run nicely (within 5%). The maximum deviation between the two parameters is observed for pyrazole, where the aromaticity of 86,1 % is calculated using NMR and 81,6 % is calculated on the basis of geometric parameters. These quantitative estimates of the flavourings of the five member heterocycles are also comparable to those of aromatic stabilisation sources. Quantification of aromatics through energy, magnetic and structural criteria may provide the same information provided that the relevant systems are selected. Conflict of interest The authors declare that there is no conflict of interest with respect to the publication of this article. AcknowledgementsKhurshid Ayub highly recognises the Higher Education Commission of Pakistan (Grant no. 1899 via no. 20-1899/R&D/10/8863) for its financial support for the project. Support from the COMSATS Institute of Information Technology and King Faisal University is also highly appreciated. Additional MaterialsStylitary coordinates of optimized geometry are available in the secondary material. Image copyright © 2015 Maria and Khurshid Ayub. 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